

A STUDY OF ELECTRODE PHENOMENA

BY

THE CATHODE RAY OSCILLOGRAPH.

by

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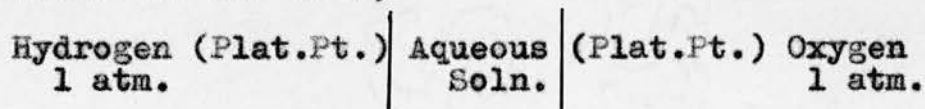
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Part I.

The anodic and cathodic polarisation
of platinum in nitrogen saturated
acid and alkaline solutions.

INTRODUCTION.

It can be shown on thermodynamic grounds that the E.M.F. of the cell,



should be about 1.2 volt, but it is usually about 1.10 volt; hence the decomposition voltage of any aqueous solution from which the products are hydrogen and oxygen should be 1.1 volt approximately. With smooth platinum electrodes the decomposition voltage is actually 1.7 volt, hence the electrode material introduces an irreversibility or polarisation effect.

Caspari⁽¹⁾ in 1899, made a systematic study of the potential at which hydrogen was evolved at various metal electrodes in dilute sulphuric acid solution. In all cases, except that of platinised platinum, an excess negative potential was required before hydrogen evolution

commenced. The difference between the actual potential at which visible bubble evolution commenced and the thermodynamically reversible value was called the "Overvoltage". He succeeded in placing the metals in a series of increasing overvoltages, and this series corresponds to the order of activity of the metal in catalysing reactions in which hydrogen takes part.

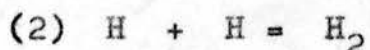
Haber⁽²⁾ also studied this phenomena and came to the conclusion that the hydrogen overvoltage was caused by a gas film obstructing the passage of ions from the solution to the electrode.

The concept of overvoltage was extended by Tafel⁽³⁾ who measured the difference between the potential of an electrode at which hydrogen was being evolved by electrolysis at a definite current density and that of a reversible hydrogen electrode in the same solution. The variation of the overvoltage with the current can be represented by the following equation:-

$$I = ke^{-bV}$$

where I is the current density, V the overvoltage, and b and k constants. Tafel found that b was approximately equal to $F/2RT$, where R is the gas constant and F the electrochemical equivalent.

According to Tafel the liberation of molecular hydrogen occurs in two stages:-



If either of these stages occurred slowly the process

would not be thermodynamically reversible. Hence there would be no hydrogen evolution at the reversible potential, any retardation of the discharge of hydrogen ions to molecules would therefore, result in polarisation. Tafel considered that the first stage took place with extreme rapidity and that the second stage was the slow one, which resulted in the accumulation of atomic hydrogen at the cathode. Tafel supposed this atomic hydrogen was electromotively active and set up a potential difference according to the Nernst formula :-

$$E = E - \frac{RT}{F} \log \frac{C_H}{C_{H^+}}$$

where C_H and C_{H^+} represent the concentrations of atomic and ionic hydrogen. Now the value of C_H in the vicinity of the electrode will be determined by, (1) its rate formation and (2) its rate of combination to form free molecules.

According to Tafel we have,

$$-\frac{dC_H}{dt} = K(C_H)^n$$

In the stationary state

$$I = K(C_H)^n$$

$$C_H = K^n \sqrt[n]{I}$$

$$E = E - \frac{0.057}{n} \log I$$

where $E = E - \frac{RT}{Fn} \log \frac{1}{C_{H^+}}$

or $E = a - \frac{0.057}{n} \log I$

where n cannot be less than 1.

If the reaction is a bimolecular one, as might be expected, $n = 2$ and this calculation gives $b = 0.029$, which is only a quarter of the experimental value. So the theory is unable to account for the slope of the $E/\log I$ curves.

Of the numerous other theories put forward, it is impossible to mention more than a few.

Attention has been repeatedly drawn to the parallelism of the order of the overvoltages of metals with the catalytic power. The most significant paper is that by Bonhoeffer⁽⁴⁾, who investigated the catalytic action of metals on the combination of atomic hydrogen in the gaseous state. He found a general agreement between the catalytic power and the hydrogen overvoltage of metals.

The hydrogen overvoltage has also been regarded as a measure of the energy required on account of surface forces to form gas bubbles from a supersaturated solution. The work of Glasstone⁽⁵⁾ may be taken as typical of this view.

Some authors consider that more or less definite hydrides are formed at the cathode.⁽⁶⁾ This view is based on the observation that cathodic hydrogen frequently contains known hydrides e.g. at antimony and arsenic and carbon electrodes. It is possible, however, that hydride formation may be a consequence of a high overvoltage rather than the cause of it. Another theory

which is of interest because of its unusual^u nature has been suggested by Smitts,⁽⁷⁾ on the basis of his theory of allotropy..

In Tafels relation,

$$I = ke^{-bV}$$

the constant b , is approximately equal to $F/2RT$. This value has been verified by Bowden⁽⁸⁾ and by Harkins⁽⁹⁾. Bowden has also shown the dependence of the constant b on the temperature as required by the relation $b = F/2RT$. This relationship also holds for the liberation of oxygen at the anode.

In the theories which have been previously mentioned, it has been assumed that the process $H^+ + e = H$, takes place instantaneously and has no effect on the overvoltage. It was assumed that this transfer can occur at any rate fixed by the current density, and at the reversible hydrogen potential. The conditions, however, under which electrons may be transferred from an electrode to reducible substances in solution or adsorbed on the electrode surface were first examined by Butler.⁽¹⁰⁾ Butler supposed that the existence of a potential difference V , at the surface effectively reduced the thermionic work function ϕ , at the cathode to $\phi - V$. The rate of transfer of electrons from the metal to reducible molecules of concentration x at the surface is given by :-

$$I = Kxe^{-(\phi + FV)/RT}$$

According to this equation a displacement of the potential difference from the reversible value would be a necessary condition for the passage of a current. The factor $dV/d \log I = RT/F$ is however only half that required for the measurement of the hydrogen overvoltage.

Erdey-Gruz and Volmer,⁽¹¹⁾ who made use of a similar equation supposed that before escaping from the metal and neutralising hydrogen ions in solution, electrons must acquire an activation energy U . In the absence of a potential difference the number escaping is :-

$$I = Kc^+ e^{-U/RT}$$

where c^+ is the concentration of hydrogen ions in the electrical double layer. They suppose that only a fraction α , of the potential difference at the surface, was effective in modifying this rate and gave an equation:-

$$I = Kc^+ e^{-(U + \alpha FV)/RT}$$

Which is in accordance with experiment if $\alpha = 0.5$.

Gurney⁽¹²⁾ has examined the quantum mechanics of the transfer of electrons between an inert metal electrode and ions in solution. Gurney has shown that a relation of the type given by Tafel may arise from the conditions of the transfer.

According to Gurney the conditions for the transfer of electrons to positive ions in solution, or from

negative ions to the electrode are, $E_+ > \phi + V$, $E_- < \phi + V$ respectively.* is the thermionic work function of the metal and E_+ , E_- the neutralisation potentials of the ions. In the extended form of the theory these are defined as $E_+ = I_+ - W_+ - R_+$, $E_- = I_- + W_- + R_-$, where I_+ , I_- are the ionisation potentials of the ions, W_+ , W_- the hydration energies of the ions, and R_+ , R_- quantities representing the repulsive energy between the solvent and the ion after neutralisation.

By integrating the probabilities of transfer between ions for which these conditions are satisfied, he obtains on certain assumptions $I = k'Te^{\pm FV/2RT}$ where the positive sign refers to the discharge of negative ions and the negative sign to positive ions.

According to this calculation, the rate of transfer of electrons from the electrode to hydrogen ions in solution at the reversible potential V is:-

$$I = k'Te^{-FV/2RT}$$

As pointed out by Gurney, the process of electron transfer is essentially irreversible, for the reverse transfer of electrons from either free hydrogen atoms or molecules cannot occur to an appreciable extent in the same potential region.

An alternative mechanism has been suggested by Horiuti and Palanyi⁽¹³⁾ in which the primary process is the transfer of hydrogen ions to adsorption positions

* The convention with regard to the sign of the potential used here is opposite to that employed by Gurney.

on the metal surface, in the course of which neutralisation occurs. This process may under certain circumstances be reversible, but on the assumptions made has a high activation energy.

In a recent paper by Butler,⁽¹⁴⁾ a scheme has been suggested which contains features from the theories of Gurney, and Morvuti and Polanyi. The theory put forward can apply to reversible and irreversible electrodes. In this theory account is taken of the adsorption energy of hydrogen atoms on the metal, and shows how as a result, the adsorption of hydrogen on the metal surface may take place at a lower potential than is required for the liberation of free hydrogen.

It is also shown that the activation energy of the process can be so reduced, as to make reversibility highly probable. At the reversible hydrogen electrode, not only must the process of hydrogen adsorption be reversible, but the adsorbed hydrogen must be in equilibrium with the atmosphere of gaseous hydrogen. From a consideration of this fact, Butler shows that so long as the current is small, the rate of liberation of hydrogen is determined by the rate of combination of hydrogen atoms to form molecules, (or by the rate of dissociation to molecular hydrogen to form atoms). At high current densities, however, the rate determining step is the neutralisation of hydrogen ions, such as we have in Gurney's process, which applies to the liberation

of hydrogen at high overvoltage metals.

Butler points out, that so far no evidence has been obtained to show that the adsorption of hydrogen takes place on bright platinum electrodes below the normal overvoltage. Most of the experiments on the hydrogen overvoltage have, however, been carried out in solutions saturated with hydrogen, after the electrode has been given a preliminary cathodic polarisation to remove traces of oxygen. The adsorption of a layer of oxygen at anodes has, however, been shown to take place before the normal oxygen overvoltage has been reached. (15, 16)

The object of the experiments which I am about to describe has been to see if it can be demonstrated, that with a bright platinum electrode, the adsorption of a layer of hydrogen atoms takes place before the normal overvoltage is reached. Frumkin and Sygin⁽¹⁷⁾ have shown that this is the case with platinised platinum electrodes.

A study of the anodic and cathodic behaviour of platinum in acid and alkaline solutions, saturated with nitrogen, was therefore undertaken. Such experiments have been carried out in hydrogen saturated solutions by Butler and Armstrong, (18) and by Bowden. (19)

These workers used currents of the order of 1 to 30×10^{-3} amps/cm². At these currents the process is relatively slow, and diffusion effects may mask the process actually occurring at the electrode surface.

The present series of experiments were carried out with high current densities of the order of 300 to $4000 \times 10^{-3} \text{ amp/cm}^2$. With such large currents the process is complete in less than $1/300\text{th}$ sec. Such short times rule out the string galvanometer as a recording instrument, since the period is of the order of $1/200\text{th}$ sec. The changes of electrode potential with time were therefore recorded by a cathode ray oscillograph, used in conjunction with a large aperture camera. The apparatus will be fully described in the experimental section.

EXPERIMENTAL.Methods of measurementRapidly changing potentials.

The rapid variations of the electrode potential with time were recorded photographically by means of a cathode ray oscillograph used in conjunction with a large aperture reflex camera. The essential parts of the oscillograph circuit are shown in fig I.

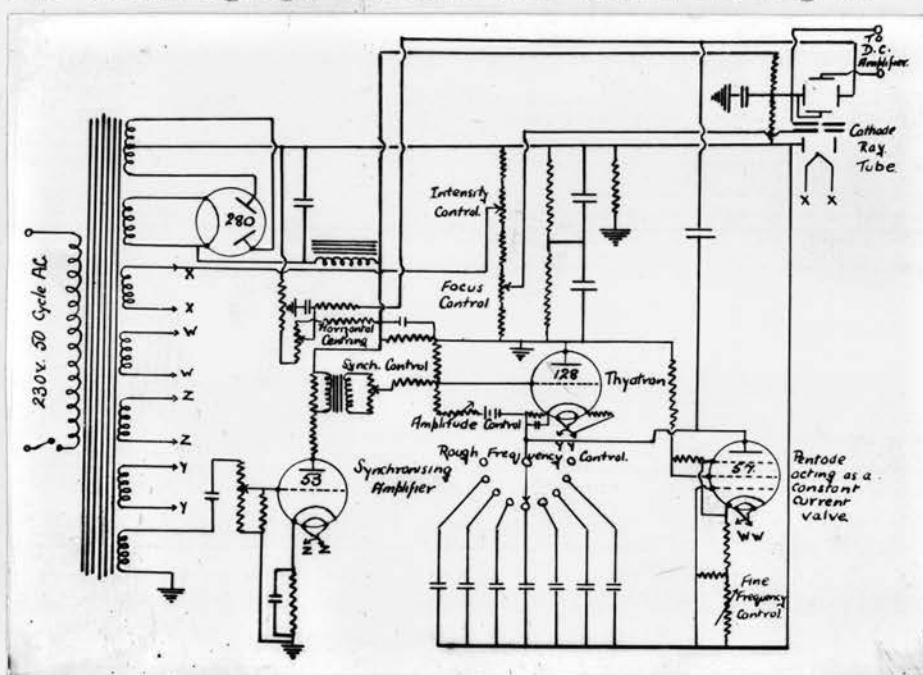


Fig. I.

The horizontal deflection plates of the cathode ray tube are connected to a linear time base, the frequency of which can be varied from 10 to 100,000 sweeps per second. This time base consists of the thyatron valve (128), the pentode valve (57) and the associated components.

In order to obtain an unvarying sweep frequency, it is necessary to link the time base to a source of constant frequency. The 50 cycle A.C. mains, which

are time controlled were chosen for this purpose. Stable working conditions are most easily obtained when the sweep frequency is the same as that of the A.C. mains. Stable conditions can also be obtained when the sweep frequency is adjusted to multiples of 50, provided the instrument has been given sufficient time to warm up.

The sensitivity of the cathode ray tube is such that 25 volts are required to deflect the spot 1 inch. Since the maximum change of electrode potential is of the order of 2 to 3 volts, a two valve amplifier was constructed to increase the sensitivity of the cathode ray tube. (Fig II). As normally used the sensitivity of the apparatus is such that 0.1 volt change in the input voltage caused a deflection of 0.3 to 0.4 cm.

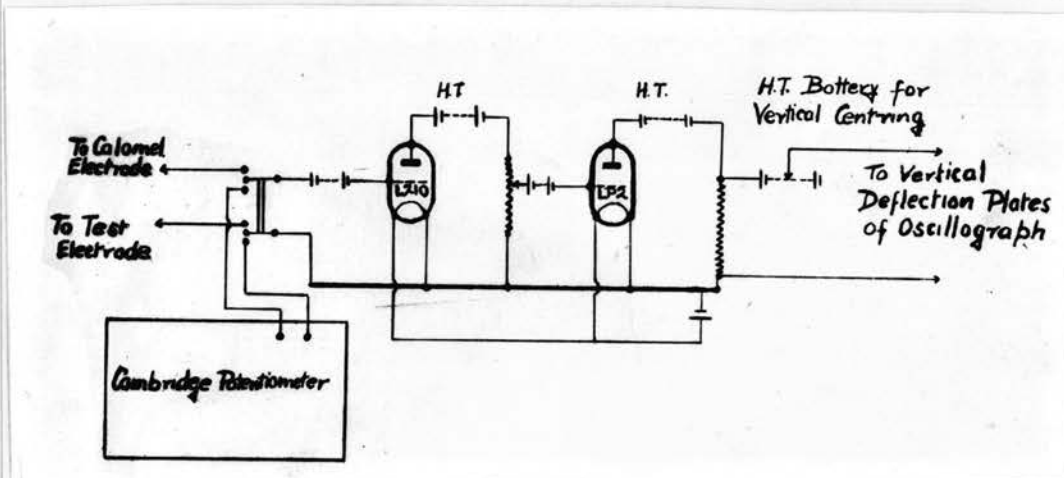


Fig. II.

The grid current taken by the initial valve of the amplifier was negligible with the grid bias used.

Fig. II also shows the arrangement of the apparatus associated with the oscillograph. By means of the change over switch it is possible to connect the input terminals of the amplifier to the test electrode and the standard half cell or to a Cambridge potentiometer for calibration purposes.

Measurement and control of the polarising current.

The arrangement for supplying and controlling the polarising current to the system is shown in fig. III.

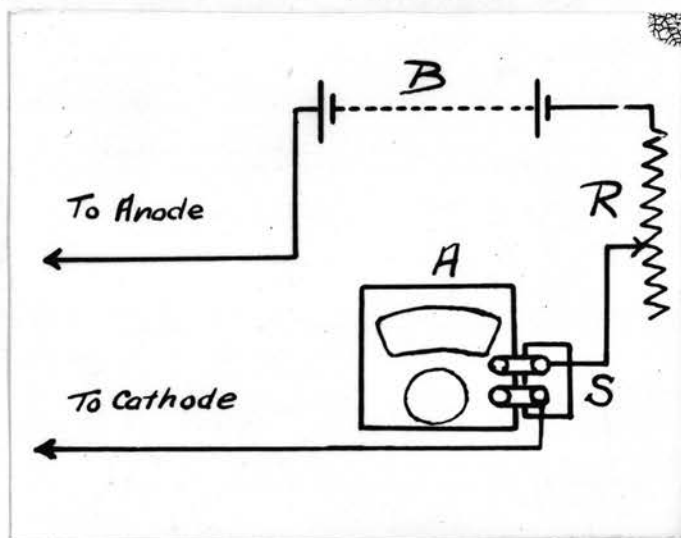


Fig. III.

The current was derived from a battery of 50 accumulators capable of giving a large current with negligible voltage variation. The current was controlled by a rheostat R and measured by a unipivot micro-ammeter. This instrument with suitable shunts had a measuring range of a few microamps to 12 amps. A reversing switch (not shown), was also included in this circuit.

When experiments were first commenced, considerable difficulty was encountered in the switching on of large currents, the switches used having a variable contact resistance.

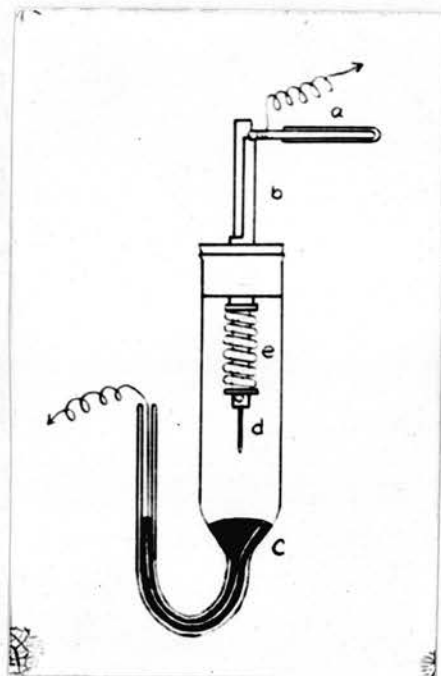
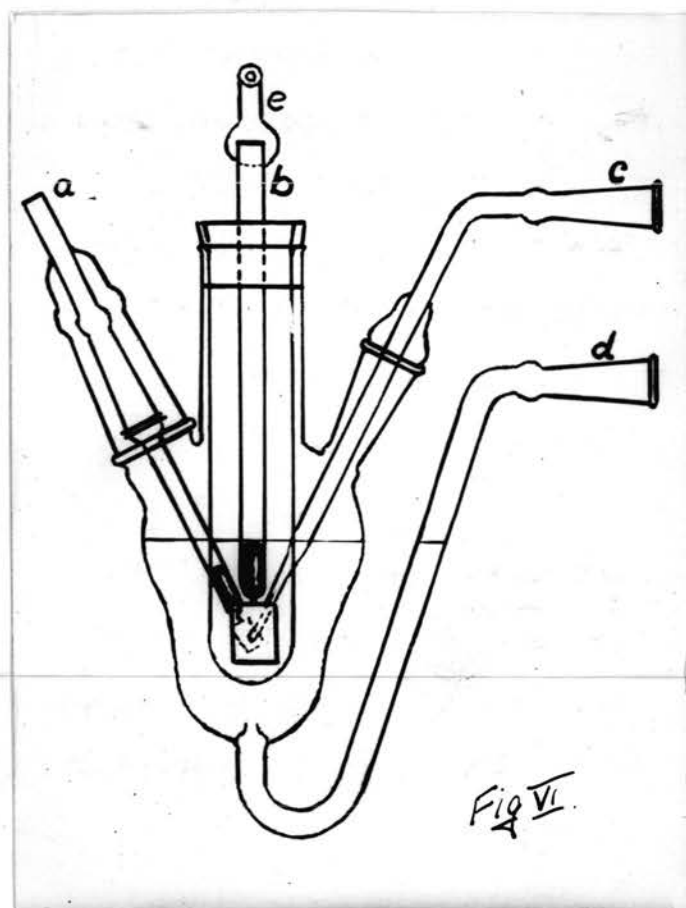
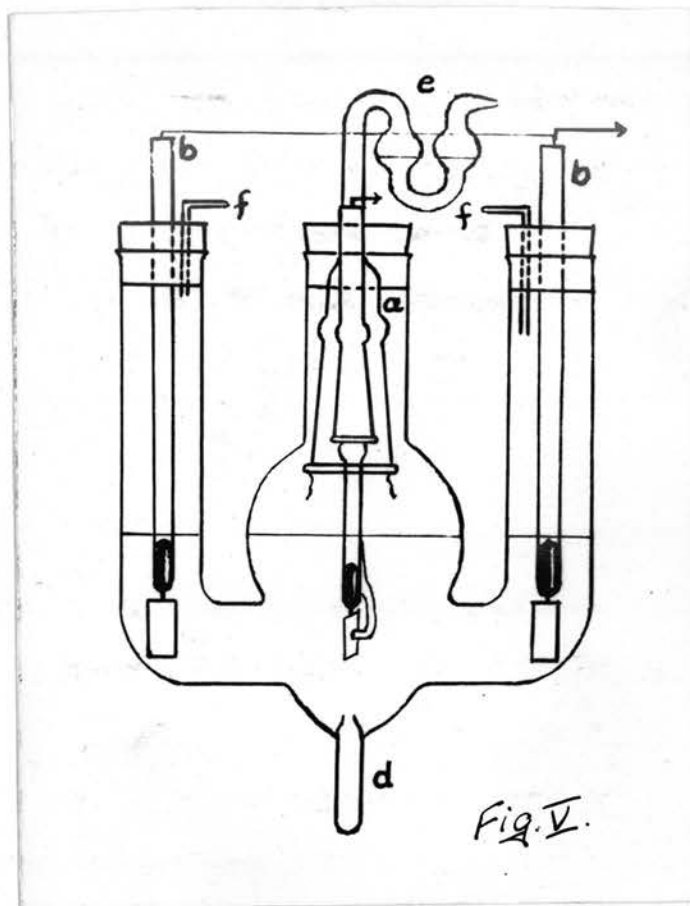


Fig. IV.

A quick acting mercury switch of the type shown in fig. IV, was made and proved quite satisfactory. The brass rod carrying the thick platinum wire d, slides easily in the brass tube b which is cut away on one side as shown. The brass rod a, has a piece of glass tubing over it. On giving a, a slight push, the brass rod carrying the platinum point plunges into the mercury at c.

Standard half cell.

The potential of the test electrode was always measured against a normal calomel electrode. The potential of the normal calomel is +0.282 volts relative



to the standard hydrogen electrode. The measured values of potential of the test electrode were reduced to the standard hydrogen scale by adding +0.282 volts.

The whole apparatus with the exception of the oscillograph, which was earthed, was insulated by sheets of glass supported on blocks of paraffin wax.

Electrolysis cell.

Figs. V and VI, give two views at right angles to each other, of the cell used. In view of the high current densities the test and auxiliary electrodes were placed in the same compartment. From the geometry of the cell it is seen that a uniform current density is obtained at the test electrode. Owing to the system of ground glass joints the test electrode a can be quickly removed and another put in its place. The electrodes used had an apparent area of 0.5 sq.cm. These were made by sealing a short piece of platinum wire into the end of a glass tube and spot welding the bright platinum foil to this. The auxiliary electrodes b had an area of 1 sq.cm. and were made in a similar way. The calomel electrode was connected via the ground glass joint g. The tip of the calomel was kept a constant distance of about 1.5 mm. from the test electrode, thus keeping the ohmic drop between the test electrode and the tip at a minimum, while at the same time causing as small a disturbance at the

electrode as possible. Nitrogen was bubbled into the cell via d. The nitrogen escaped via the gas trap e. The gas liberated at the auxiliary electrodes escaped via the narrow tubes f,f.

Purification of nitrogen.

The nitrogen, obtained from a cylinder, was passed over a copper spiral heated in an electric furnace and then through a solution of alkaline pyrogallate.

Preparation of solutions.

The electrolyte was prepared from A.R. sulphuric once distilled in a pyrex apparatus diluted with water also distilled in a pyrex apparatus. 1.0N sulphuric acid solution was used in all the experiments.

Summary of Bowdens experiments.

Before describing the results of the present research it is necessary to summarise the work of earlier investigators.

Experiments have been carried out by Bowden⁽¹⁹⁾ on the anodic and cathodic behaviour of platinum in hydrogen and oxygen saturated sulphuric acid solutions. The current densities were of the order of $10 - 25 \times 10^{-3}$ amps/c.m.² The following is a summary of his observations.

Platinum electrodes in M/10 sulphuric acid saturated with hydrogen.

If the electrode be made cathodic, the cathode potential changes linearly with time, and the quantity of electricity required to establish the hydrogen over-voltage is about 1.8×10^{-5} couls.per.volt increase for platinum electrodes of 1 sq.cm. apparent area. Comparison with the same quantity for mercury electrodes showed that the platinum electrodes had an effective area of 3 sq.cm, if it can be assumed that the mercury surface is perfectly plane.

On making the platinum electrode anodic after a cathodic polarisation, the potential falls rapidly to the reversible hydrogen potential, then linearly from this value to +2.0 volts (corresponding to a considerable oxygen overvoltage), with a slight pause at +0.61 volt. (See fig.VII curve I). Excluding the arrest at 0.61 volt, 3×10^{-3} couls. are required to produce the change.

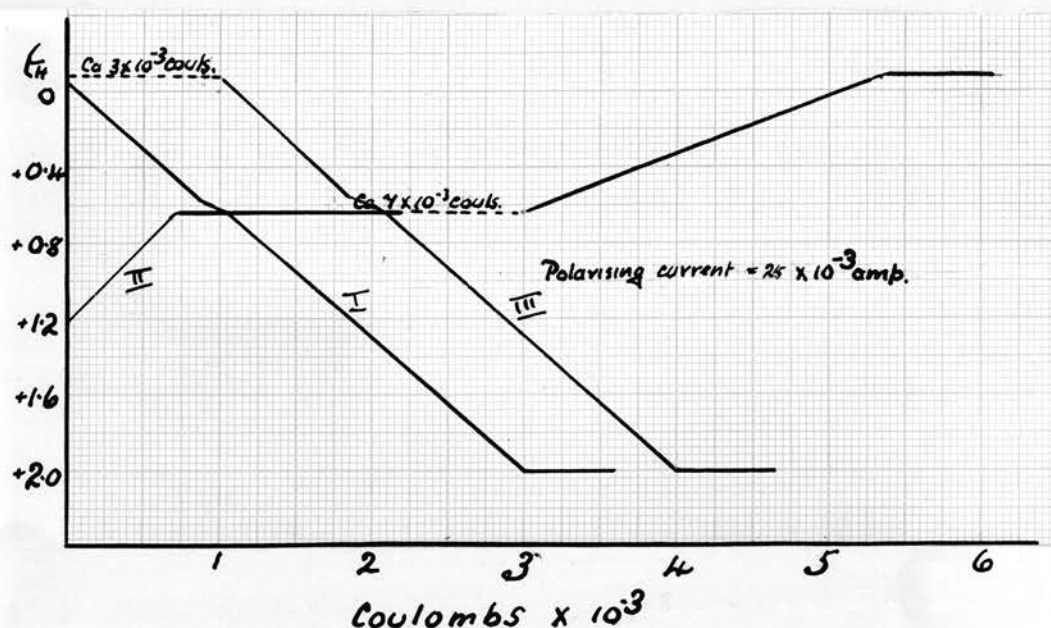


Fig. VII.

On stopping the anodic current, the electrode potential rises rapidly to +1.4 volt and then more slowly. If at this point the current is reversed, the potential rises linearly to +0.61 volt and remains constant while 7×10^{-3} couls. are passed. The potential then rises again, and after 2.4×10^{-3} couls. are passed, reaches the reversible hydrogen value (fig.VII curve II). Excluding the arrest at +0.61 volt, the quantity of electricity for the change is 3.2×10^{-3} couls.

An electrode, which has been made anodic several times, differs from an electrode which has never been made anodic. On making the electrode anodic, it tends to remain at the reversible hydrogen potential and then changes to the oxygen overvoltage in the usual way. (fig.VII curve II)

Platinum electrodes in M/10 sulphuric acid
saturated with oxygen.

The quantity of electricity required to establish the oxygen overvoltage is 3.8×10^{-4} couls. per volt increase for an electrode of 1 sq.cm. apparent area.

On making the electrode cathodic, the potential falls linearly to about +0.62 volt, and the amount of electricity required for the change is 1×10^{-3} couls. The potential remains constant at 0.62 for a time depending on the length of the previous anodic polarisation, then passes to the reversible hydrogen value.

If, after cathodic polarisation, the circuit is opened, the potential falls to +0.87 volt., after remaining for a short time at the reversible hydrogen potential.

Bowden considers that the values +0.61 volt and 0.87 volt are the equilibrium potentials of an oxide of platinum in contact with hydrogen and oxygen saturated solutions. +0.61 would probably represent the reduction potential of the oxide to platinum and water. It is also suggested that the change of potential from the hydrogen to the oxygen reversible value, or vice versa, involves the removal and subsequent deposition of a layer of gas adsorbed on the accessible metal atoms in the electrode surface. For this a constant quantity of 3×10^{-3} couls. is required.

Summary of experiments by Butler and Armstrong (18)

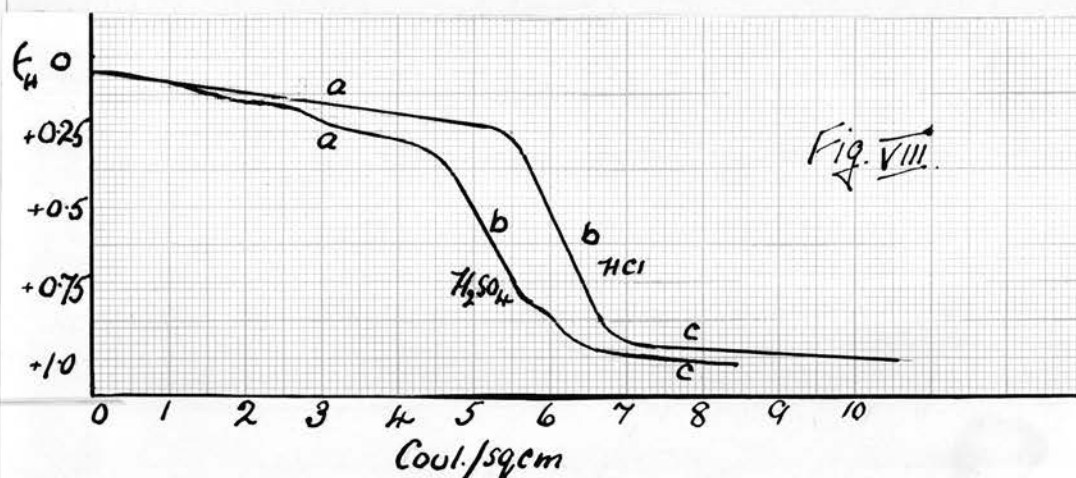
Experiments were carried out on the anodic and cathodic polarisation of platinum electrodes in solutions saturated with hydrogen and oxygen, using current densities between 0.5 and 30×10^3 amps/sq.cm.

On the anodic polarisation of electrodes, which have been given an initial cathodic polarisation in hydrogen saturated solutions, two depolarisation processes are observed at potentials more negative than that at which the steady liberation of oxygen occurs. They are ascribed respectively, to the electrolytic dissolution of adsorbed or dissolved hydrogen, and to the formation of a layer of adsorbed oxygen. These processes take place at +0.4 and +1.2 volts respectively.

On cathodic polarisation of an electrode which has been previously anodically polarised one such process is observed which marks the removal of the adsorbed layer of oxygen. These authors show that, contrary to the views of Bowden, no platinum oxide is formed on the anodic polarisation of platinum in sulphuric acid solution.

Summary of experiments by Frumkin and Slygin. (17)

Experiments were carried out with platinised platinum electrodes in sulphuric, hydrochloric, and hydrobromic acid solutions, at current densities of 1.0×10^{-4} amps/cm.² Initially the solution was saturated with hydrogen, nitrogen was then passed through the solution to remove the hydrogen. The hydrogen saturated electrode was thus left in a hydrogen free solution. The electrode was now made anodic and the type of curve obtained is shown in fig.VIII.



According to the authors, we have, on anodic polarisation the removal along a of a layer of adsorbed hydrogen. The quantity of electricity passed along b represents that required to alter the capacity of the electrical double layer, while along c the deposition of oxygen takes place. The curve is completely reversible provided the electrode is not taken too far into the oxygen deposition region. Similar curves were obtained with the other acids as electrolytes.

These experiments have the disadvantage that the

precise nature of the electrode surface is not known.

Experimental procedure.

Two methods were used to give the electrode the initial cathodic or anodic polarisation before taking the anodic or cathodic curve.

(1). When it was undesirable to release oxygen or hydrogen at the test electrode, the anodic or cathodic polarisation was carried out by a small current, usually a few microamperes, the potential of the electrode being observed by a string electrometer. By this method it was possible to take the electrode to any desired potential before taking the anodic or cathodic curve. The electrode having attained the required potential, the cathode ray intensity control was increased to maximum, (the sweep frequency having been previously adjusted to a suitable value), the camera shutter opened and the large anodic or cathodic current switched on. The resulting trace was thus photographed and the camera lens capped. The curve was now calibrated. A mask with a vertical slit 2mm. wide was placed over the end of the cathode ray tube, and the amplifier input terminals connected to the potentiometer. The 0.1 volt ratio dial of the

potentiometer was now rotated, the cap having been previously removed from the camera lens. This gave a series of lines on the negative, the distance between each line corresponding to 0.1 volt. This method of will be referred to as the controlled polarisation method.

(2). When the liberation of oxygen or hydrogen at the test electrode was not objectionable, the anodic or cathodic polarisation was carried out with a large current usually of the same magnitude as that with which the cathodic or anodic curve was to be taken.

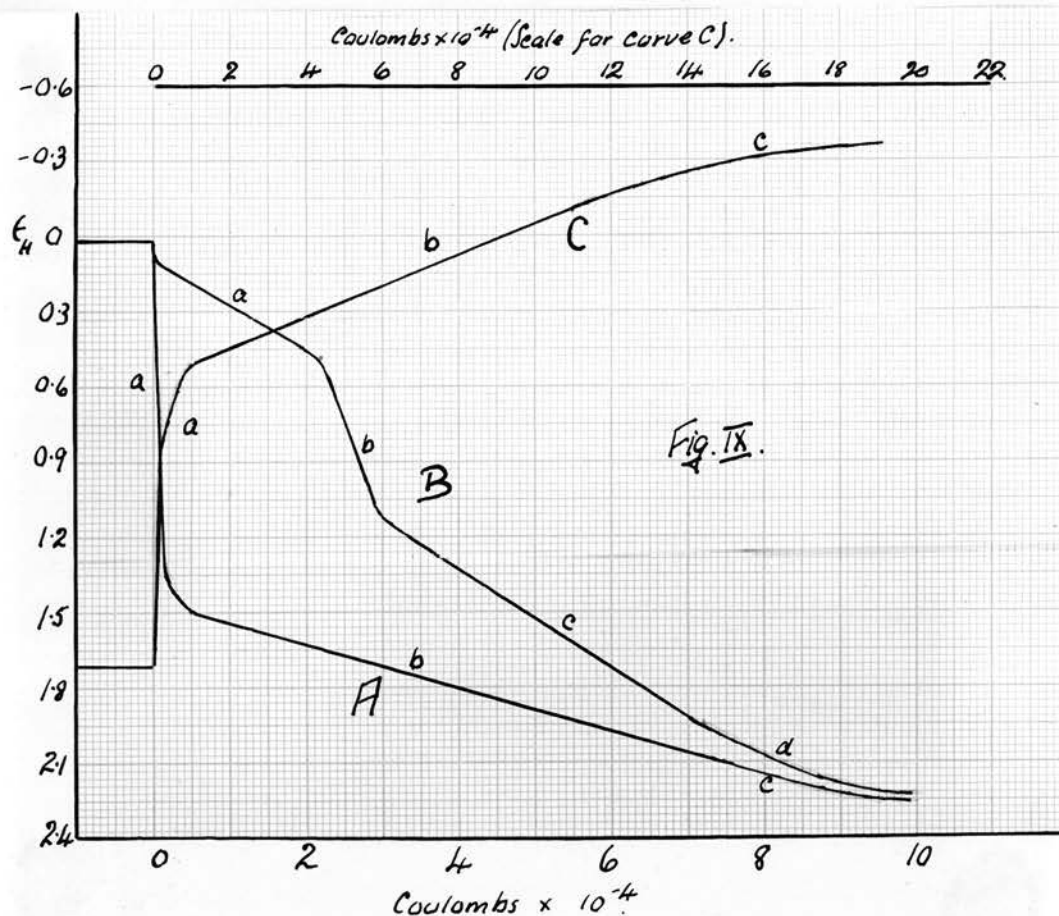
Nitrogen was passed for 5 minutes after each curve was taken.

Experiments with platinum electrodes in normal sulphuric acid saturated with nitrogen

Experiments using second method of polarisation

After a preliminary cathodic polarisation, two types of curves were obtained on making the electrode anodic. Curves of type A, fig IX, were obtained with new electrodes which had not previously been made anodic, or with electrodes which had been left in the solution for some time (one day or over). After a cathodic polarisation the electrode remained at the reversible hydrogen electrode potential. On application of the large anodic current the electrode potential

fell rapidly to about +1.5 volt. The linear stage b then commenced, the potential falling to +2.1 volt, after which the curve ceased to be linear, oxygen being liberated at c. The potentials mentioned are dependant on the anode current, the larger the current the more positive the potentials. Those given are for a current of 0.6 amp. corresponding to a current density of 1.2 amp/cm.²



An electrode which had previously been made anodic gave curves of type B. On application of the anodic current the electrode potential fell instantaneously

to +0.08 volt. The electrode potential then fell more slowly, giving rise to the linear stage a. At +0.5 volt the fall became more rapid but remained linear, giving rise to stage b. At +1.1 volt the rate of fall in potential became less, giving rise to stage c. At +1.9 volt the fall ceased to be linear, the potential finally reaching the constant value of +2.3 volt.

The slopes of the linear portions a and c of the curve are approximately the same, while the quantity of current passed along section c is twice that along a. Also the quantity of current passed along the linear portions of the curves A and B is independent of (1), the initial cathodic polarisation, which was varied from 2×10^{-2} to 6 couls, and (2), the current density over the range 200×10^{-3} to $4,000 \times 10^{-3}$ amps/cm².

The quantity of current passed along section b of curve B is 8×10^{-5} couls., the slope being 1.4×10^{-4} couls/volt. These values are of the order one would expect for a change in the capacity of the electrical double layer in this region.

The mean value of the current passed along section a of curve B is 2.4×10^{-4} couls, while that for section c is 5.1×10^{-4} couls. These values are the mean of a number of determinations with different electrodes. The results are tabulated in table I.

With regard to curve A, it is found that the amount of current passed along the linear part of the

Table I.

Electrode	Section <u>a</u> couls $\times 10^{-4}$	Slope couls/volt $\times 10^{-4}$	Section <u>c</u> couls $\times 10^{-4}$	Slope couls/volt $\times 10^{-4}$
E	---	---	6.4*	7.0
	2.5	6.5	6.7	7.5
	2.6	---	5.6	6.2
	2.6	6.5	5.0	7.6
D	---	---	9.4*	12.0
	---	---	5.4	6.5
	2.5	6.0	5.5	---
B	---	---	7.4*	12.0
	---	---	8.0*	8.0
	2.6	6.5	5.6	6.2
	2.5	6.5	4.7	5.3
	2.3	6.0	5.0	7.3
G	---	---	4.1*	8.0
	1.8	---	4.1	5.0
	---	---	3.9	5.0

*The values marked thus are for the electrodes in the inactive state and represents the quantity of current passed along section b of curve A.

curve is approximately equal to the sum of that passed along stages a and c of curve B, namely 7.2×10^{-4} couls.

Cathodic curves after large anodic polarisations.

Fig.IX, curve 6, shows the type of curve obtained after a preliminary anodic with a large current. After the anodic polarisation the electrode potential rises rapidly from 2.2 volt to 1.4volt at which it remains stationary. On application of the cathodic

current the electrode potential rises rapidly to +0.5 volt. A linear stage b now commences and the electrode rises to -0.1 volt, after which it rises more gradually to the final potential of -0.4 volt. These voltages are for a current of 0.6 amp., with larger currents more negative values are obtained.

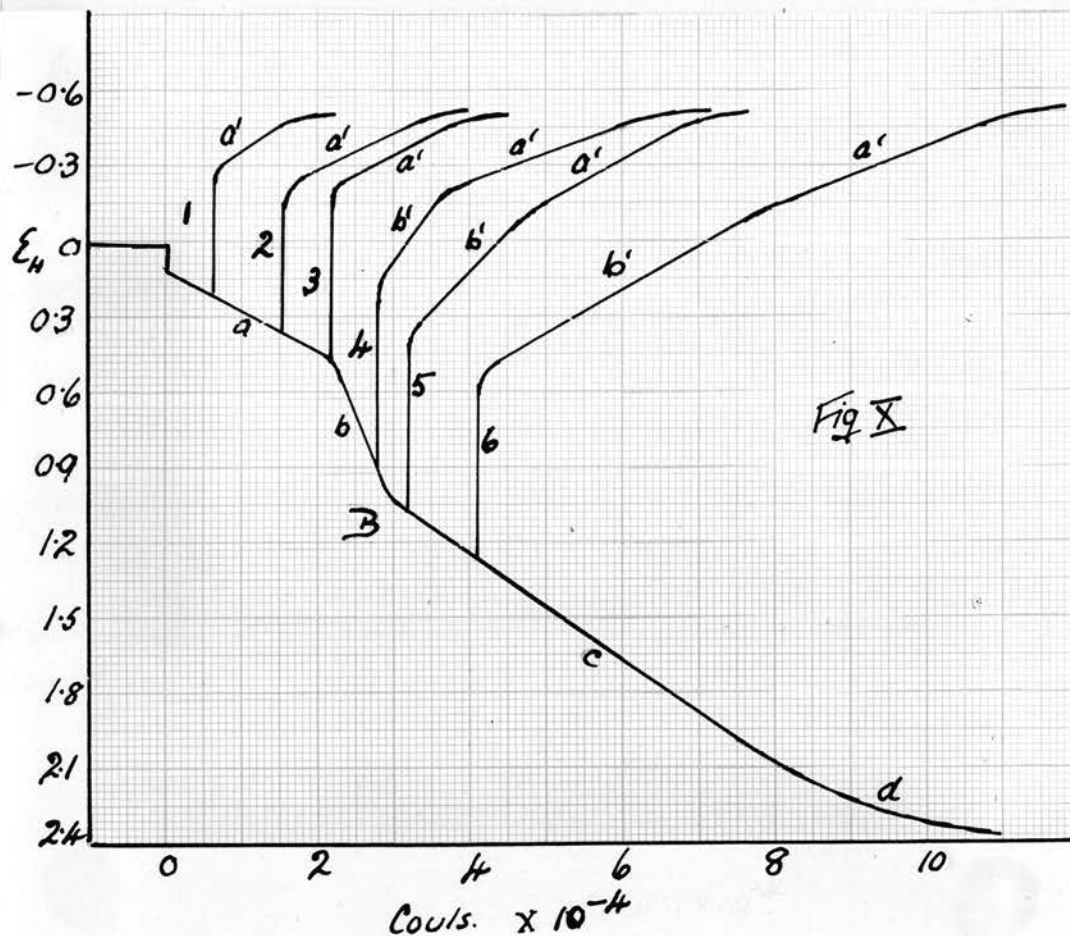
Table II

Electrode	Section <u>b</u> couls x 10^{-4}	Slope couls/volt x 10^{-4}
E {	9.5	13.0
	11.0	15.0
	10.4	17.6
D {	9.7	14.0
	14.0	20.0
B {	12.5	25.0
	10.0	20.0
	9.3	19.0
	10.0	17.0
G {	8.0	13.0
	8.6	13.6
	8.6	12.0

The quantity of current passed along the linear part b of the cathodic curve is of the order of 10.0×10^{-4} couls. (Table II).

The slope of the upper part of a is probably not far different to the slope of b curve B, and this change consists of the practically instantaneous rise of potential on starting the current followed by a normal capacity effect.

Cathodic curves taken after anodic polarisation under controlled conditions.



The results of these experiments are shown in fig.X. The anodic polarisations were carried out with a current density of 10 microamps. Curves 1 to 6 show the effect to taking the electrode to increasingly positive potentials before taking the cathodic curve. Curve A is a typical anodic curve and is inserted in the figure for the purpose of comparison. Curves 1, 2, and 3 demonstrate the gradual growth of the stage a' on the cathodic curve as the electrode is taken to more positive values on the initial anodic polarisation.

The initial potential change in curves 1 to 3 is instantaneous, and is probably the result of the ohmic resistance of the solution between the test electrode and the tip of the calomel electrode.

Curve 4, shows the appearance of the capacity change stage b^* . This is to be expected since the capacity change section of the anodic curve B has been entered during the initial anodic polarisation. The quantity of current passed along b' is equal to that along b , while the slopes are similar.

In the case of curve 5 the amount of current passed along b' is greater than along b . This is due to the fact that the initial potential of the electrode was such that the electrode was in section c of the anodic curve. Curve 6 was taken from a still more positive potential and b' is now considerably greater than b . It therefore appears that the reverse of the process which occurs along section c of the anodic curve, (which will be shown to be the deposition of oxygen), occurs along b' concurrently with the capacity change effect. The amount of current passed along a' remains constant once a is completed.

The data from which the cathodic curves 1 to 6 were constructed is given in table III.

Table III

Initial potential	Section a' couls $\times 10^{-4}$	Slope couls/volt $\times 10^{-4}$	Section b' couls $\times 10^{-4}$	Slope couls/volt $\times 10^{-4}$
+0.23	1.0	10.3	----	----
+0.4	1.0	4.9	----	----
+0.4	1.6	8.0	----	----
+0.5	1.33	5.3	----	----
+0.95	1.87	7.5	0.93	2.34
+1.1	2.65	7.45	1.65	3.49
+1.1	2.05	7.75	1.02	2.17
+1.15	2.08	9.15	2.89	5.62
+1.3	2.66	13.3	3.94	7.6

Experiments with platinum electrodes in normal sodium hydroxide solution, saturated with nitrogen.

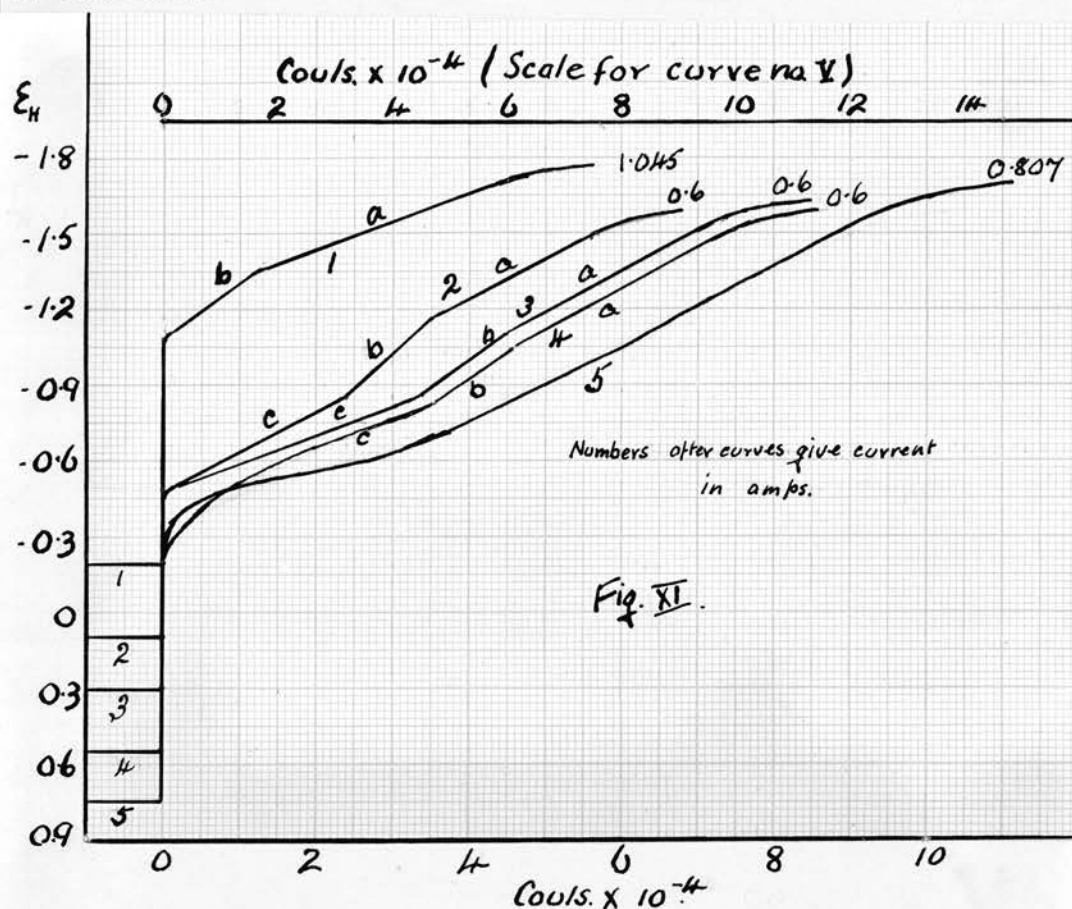
The normal sodium hydroxide solution as prepared from A.R. NaOH and distilled water.

Cathodic behaviour of platinum in sodium hydroxide solution.

The curves obtained in alkaline solution are displaced to more negative values compared with the corresponding curves in acid solution by 0.7 to 0.8 volts. This displacement corresponds to the difference between the reversible potentials of the hydrogen and oxygen electrodes in the two solutions.

After large anodic polarisations, cathodic curves of type V, fig XI, were obtained. After a large anodic the potential rose to +0.8 volt. On application of the large cathodic current the potential rose instantaneously to -0.2 volt. A slow stage then commenced and the potential rose to -0.9 volt. The electrode potential then rose more rapidly to -1.9 volt. This portion of

the curve was more or less linear. This curve differs considerably from that obtained in acid solutions, the reason being the greater activity of oxygen in alkaline solution. This is responsible for the initial slow stage on the cathodic curve, i.e. the current is still too small to eliminate the diffusion of oxygen to the electrode.

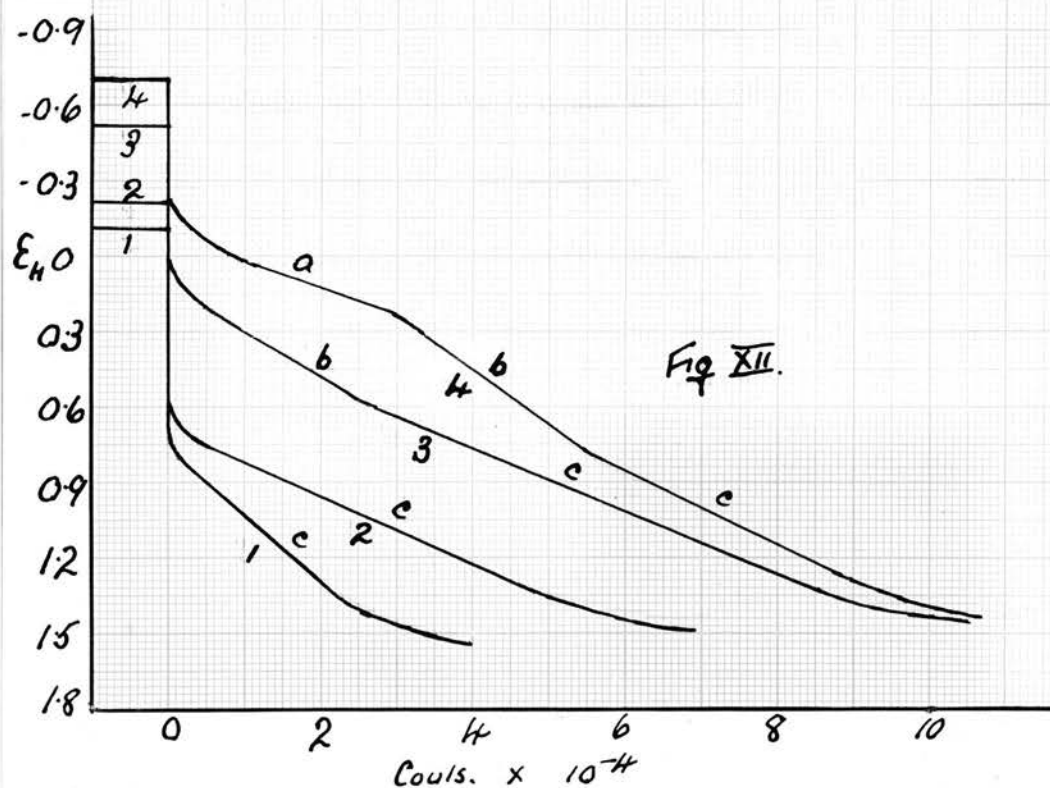


Curves I, II, III, and IV, were obtained after initial anodic polarisations under controlled conditions to potentials of -0.2, +0.1, +0.3, +0.55, respectively. Curve I. is made up of two linear stages a and b. The quantity of current passed along these stages is 3.1 and 1.1×10^{-4} coulombs, respectively.

Curves II, III, and IV show an extra stage c, the length of which increases as the initial potential of the electrode is made more positive. The quantity of current passed along stages a and b is constant and of the same value as that passed along the corresponding stages of curve I. If the initial potential of the electrodes is made more positive than +0.6 volt, the stages c and b cease to be linear and we have a gradual change in shape until finally curves of type V are obtained.

Anodic behaviour of platinum in alkaline solution.

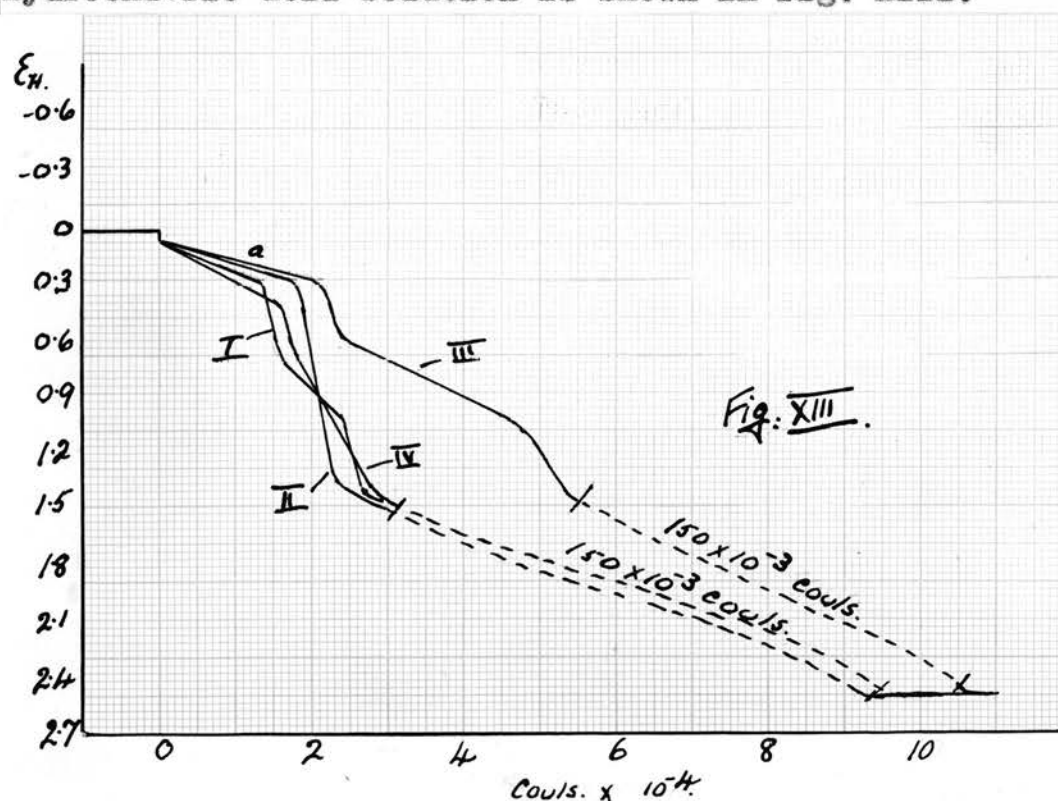
Experiments were also carried out on the anodic behaviour of platinum in alkaline solution. Some typical curves are shown in fig. XII. Curves I to III were obtained after cathodic polarisations to various potentials.



Curves of type IV were obtained after large cathodic polarisations. Along stage a, 3.0×10^{-4} couls, are passed. 2.2×10^{-4} couls, are passed along stage b. This value appears to be too large to represent a capacity change, and it is possible that some other process occurs concurrently with the capacity change. Along c, 3.2×10^{-4} couls. are passed. This is considerably less than the 5.1×10^{-4} couls. which are passed along the corresponding stage in acid solution. The anodic curve in alkaline solution departs from linearity much sooner than is the case in acid solution. The slope of curve c is however the same as in acid.

Platinum in hydrochloric acid solution saturated with nitrogen.

The anodic behaviour of platinum in normal hydrochloric acid solution is shown in fig. XIII.



Owing to the fact that the test and auxiliary electrodes were not separated by a partition impervious to chlorine, the solution at the test electrode always contained a trace of chlorine, the chlorine being released at the auxiliary electrodes during the cathodic polarisation of the test electrode.

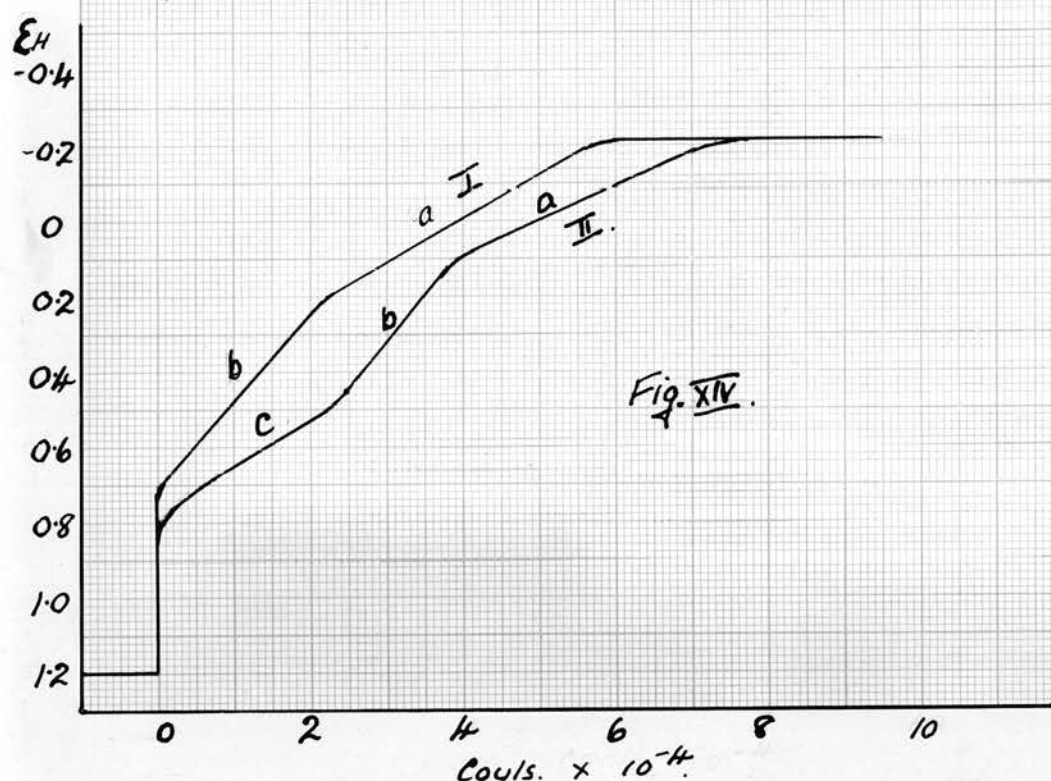
After an initial cathodic polarisation stage a appears on all curves, but its length is more variable than in sulphuric acid. This is probably due to the dissolved chlorine, which acts as a depolariser. The average value of the amount of current passed along this stage is 2.0×10^{-4} couls. This agrees fairly well with the value of 2.4×10^{-4} couls. for platinum electrodes of the same area in sulphuric acid.

The behaviour of the electrode on completion of stage a is somewhat variable and appears to depend on two factors:- (1), the amount of cathodic polarisation and (11), the concentration of chlorine in the solution. If the concentration of chlorine is large, i.e. after a series of experiments have been made in the same solution, and the cathodic polarisation is small, curves of type II are obtained. Large cathodic polarisations and low chlorine concentrations favour curves of type I and III. Curves of type IV, are obtained in chlorine free solutions after moderately large cathodic polarisations.

The final stage of the curve from +1.5 to 2.5 volt is very long considering that the current densities

used were of the order of 1 amp/cm^2 . Along this stage 150×10^{-3} couls, were passed. At 2.5 volts we have the liberation of a mixture of oxygen and chlorine. (20)

Fig.XIV shows two typical cathodic curves for platinum in normal hydrochloric.



The electrode potential rose rapidly to +1.2 volt on breaking the anodic current. On applying the cathodic current a rapid rise in potential took place to +0.8 volt. In the case of curve II this is followed by a flat stage c, whose length depends on the amount of current passed during the anodic polarisation at +0.2 the rise in potential becomes more rapid, giving

rise to stage b, stage which follows is linear and amount of current passed along this stage is independent of the length of the anodic polarisation . Stage c is absent from curve I, the length of stage a, however, is the same as that in curve II. (3×10^{-4} couls.)

Curves of type I are obtained after short anodic polarisations. Stage c of curve II appears, therefore, to be due to depolarisation by chlorine in the solution in the vicinity of the electrode.

DISCUSSION.

The experiments on the anodic behaviour of platinum have shown, that except for the capacity change, the potential change from hydrogen to oxygen is practically linear with the quantity of current passed. This is also true for the reverse process. Also this quantity is independent of the current density over the range 200×10^{-3} to $4,000 \times 10^{-3}$ amps/cm².

If we examine curve B, fig.IX in detail we find that along stage a, 2.4×10^{-4} couls are passed compared with 5.1×10^{-4} couls. for stage c. The quantity of current required to deposit one oxygen atom on the electrode is twice that required to remove one hydrogen atom. It therefore seems feasible to suppose that along a we have the removal of a layer of hydrogen atoms, which were deposited by the initial cathodic polarisation, and along c the deposition of a corresponding number of oxygen atoms. So far as the deposition of oxygen atoms before the establishment of the final overvoltage is concerned, this has already been shown to take place. (15, 16)

A calculation can be made of the quantity of current required to remove a layer of atomic hydrogen from a platinum surface. It is possible, however for the hydrogen atoms to be packed on the metal surface

in two ways, either as a complete envelope, with the atoms touching each other, or alternatively, with one hydrogen atom adsorbed on each accessible metal atom. The experimental fact that twice as much current is required for oxygen deposition than for hydrogen removal points to the latter method being the more probable. We have other evidence supporting this conclusion. The work of Davisson and Germer on the diffraction of electrons indicated that the gas adsorbed on the nickel surface followed the spacing of the nickel atoms.⁽²¹⁾ It has also been shown by Johnson,⁽²²⁾ that the adsorption of atomic hydrogen on glass reaches a saturation maximum when a complete surface layer is formed with a spacing between each hydrogen atom of about 1.6×10^{-8} cm.

The diameter of the platinum atom may be taken as 2.5×10^{-8} cm. If one atom of hydrogen is attached to each accessible platinum atom on the electrode surface, the number of hydrogen atoms on 1 sq. cm. of the electrode surface is 1.6×10^{15} atoms. It requires 2.7×10^{-4} couls. to remove these from the platinum surface as hydrogen ions. To deposit an equivalent number of oxygen atoms requires $2 \times 2.7 \times 10^{-4}$ or 5.4×10^{-4} couls.

The true area of ordinary bright platinum electrodes is according to Bowden 3 times the apparent area, while Butler and Armstrong give the true area as

2.5 times the apparent area. Taking the latter value we see that theoretically 3.3×10^{-4} couls. are required for hydrogen removal (electrode area = 0.5sq.cm.), while 6.6×10^{-4} couls. are required for oxygen deposition. These values are in quite good agreement with the experimental considering the various uncertainties in the calculation.

With regard to section b of the anodic curve, it has already been suggested that this is a capacity change. Bowden has shown that the slope of the capacity change in the hydrogen region is 6×10^{-7} couls, per sq.cm. of accessible surface for a potential change of 100 millivolts. In the oxygen region the value is 11×10^{-6} couls./cm² of accessible surface, for 100 millivolts change in electrode potential. The slope of section b is 6.6×10^{-6} couls./cm² of accessible are for 100 millivolts change in electrode potential. This value lies as is to be expected between the values given by Bowden for the hydrogen and oxygen regions.

Anodic curves of type A, fig. IX, were obtained with new electrodes which had not previously been made anodic, or electrodes which had been left in the solution for one day or over after they had been made anodic. The total current passed along the linear part of the curve A is approximately equal to the sum of that passed along sections a and c of curve B, namely 7.2×10^{-4}

couls. There are two possible explanations of why curves of type A are obtained. It has been shown by Butler and Armstrong⁽²³⁾ that making a platinum electrode anodic and cathodic a few times activates the electrode and makes it function as a reversible hydrogen electrode. New electrodes may therefore be inactive, while used electrodes may lose their activity. Hence although the electrode is covered with hydrogen as a result of the cathodic polarisation, this hydrogen is not removed at the normal potential but at a more positive potential, since the activation energy of the process is greater at an inactive electrode. The hydrogen removal probably takes place along the linear part of the curve together with oxygen deposition

Alternatively the surface of the electrode may be contaminated by some impurity, and this must be removed from the electrode surface by anodic treatment before the electrode behaves in the normal manner. The presence of the impurity on the electrode may prevent the adsorption of hydrogen. Along the linear part of A we have therefore the removal of the impurity plus the deposition of oxygen.

The cathodic behaviour of platinum in normal sulphuric acid must now be examined in the light of the theory put forward to account for the anodic behaviour.

The cathodic curve is made up of three parts. (curve C, fig. IX). The slope of the initial part of

the curve, stage a, is of the correct order for a capacity change. Along section b of the curve we have the passage of 1.0×10^{-3} couls. After the anodic polarisation the electrode will be covered with a layer of atomic oxygen. On being made cathodic this will be removed. Hence along b we have the removal of an atomic layer of oxygen. This theoretically requires 6.6×10^{-4} couls., while to deposit a layer of hydrogen requires 3.3×10^{-4} couls. It is possible that along b we have the removal of a layer of oxygen and its replacement by a layer of hydrogen. It is well known that while the reversible hydrogen electrode potential can be obtained with an active platinum electrode in a solution saturated with hydrogen, the reversible oxygen potential cannot be obtained with platinum in an oxygen saturated solution. Hence the platinum electrode may be inactive towards oxygen, and curve C would in that case be the converse of curve A.

We can now turn our attention to the cathodic curves obtained after initial anodic polarisations under controlled conditions. Curves 1, 2, and 3, show that as we move to more positive potentials along stage a of the anodic curve, more hydrogen atoms are removed from the electrode surface. On cathodic treatment, however, these atoms are replaced, as is shown by curves 1, 2, and 3, along stage a'. These curves also demonstrate quite clearly the important

fact that prior to the establishment of the hydrogen overvoltage at a platinum electrode the adsorption of a layer of hydrogen atoms takes place.

Curve 4, was taken from a still more positive potential and is composed of two sections a' and b'. The quantity of current passed along a' is approximately equal to that along b, the slopes of b' and b are also equal. Hence curve 4 is made up of a capacity change section and a section along which the deposition of a layer of hydrogen atoms occurs. Curve 5 was taken with the initial potential in the oxygen deposition section of the anodic curve, hence the electrode must have had some oxygen atoms deposited on it. There is however, no sign of a stage of the cathodic curve, corresponding to their removal. The quantity of current passed along b' is now greater than that passed along b, while that along a' is almost the same as that along a. In curve 6 which was taken from a still more positive potential, the amount of current passed along b' is now much greater than that along b, while that along a' is still the same as in curves 4 and 5.

From curves 5 and 6 we see that once the oxygen section of the anodic curve is entered, i.e. once oxygen is deposited on the electrode reversibility ceases. This fact was also discovered by Frumkin and Slygin⁽¹⁷⁾ in their experiments on platinised platinum in nitrogen saturated sulphuric acid solution.

In the case of platinised platinum, however, a considerable amount of oxygen had to be deposited before reversibility ceased, whereas with plain platinum a small quantity is sufficient. This is due to the inactivity of platinum towards oxygen in acid solution. Oxygen is more active in alkaline solution and it will be shown that a separate stage for oxygen removal appears on the cathodic curves for platinum in alkaline solution.

Fig.XI shows the results of experiments on the cathodic behaviour of platinum in nitrogen saturated sodium hydroxide solution. Curve 5 which was taken after a large anodic polarisation shows a long depolarisation stage at 0.5 volt. This is most likely due to depolarisation by oxygen in the solution. Such a stage does not occur on the corresponding curve in acid solution. Curves 1,2,3, and 4 which were taken after controlled anodic polarisations to increasingly positive potentials are also different from the corresponding curves in acid solution. Curve 1, consists of the capacity change section b and the hydrogen deposition section a, along which 1.1×10^{-4} and 3.1×10^{-4} couls. respectively are passed. Curve 2 taken from a potential of +0.15 volt shows the appearance of a new stage c. Along this section of the curve we apparently have the removal of oxygen atoms deposited during the anodic polarisation. The lengths of a and b are still the same as in curve 1.

Curves 1 and 2 also show the effect of change in current density on the process. Curve 1 taken at current density of 2.09 amps occurs at a more negative potential than curve 2 taken at a current of 1.2 amps/cm². The quantity of current passed along a and b however, is unaltered by the current changes. As we take the electrode to more positive potentials the length of section c increases, this is shown in curves 2, 3 and 4. If we take the electrode to still more positive potentials to that from which curve 4 was taken, the shape of the cathodic curve changes and becomes more like that of 5.

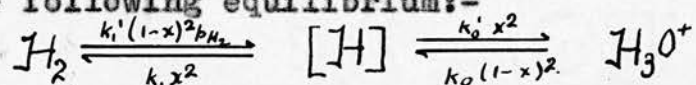
The series of curves 1 to 4 again demonstrate that prior to the establishment of the hydrogen overvoltage at a platinum electrode, the adsorption of a layer of atomic hydrogen takes place. They also show that in alkaline solution the platinum electrode is more active towards oxygen than in acid solution, as is shown by the appearance of a separate oxygen removal stage on the cathodic curve in alkaline solution.

The anodic behaviour of platinum in alkaline solution can also be interpreted on the basis of the theory which has been put forward. Curve 4 fig. XII, which was taken after a large cathodic polarisation is composed of three stages. Along a we have the passage of 3.0×10^{-4} couls. which agrees with the theoretical value for the removal of a layer of adsorbed hydrogen

atoms. Along b 2.2×10^{-4} couls. are passed. This value is too large to be entirely due to a capacity change. It is probable that owing to the relatively high activity of oxygen in alkaline solution, the adsorption of some oxygen takes place along this stage. 3.2×10^{-4} couls. are passed along c, representing the adsorption of half a layer of oxygen atoms. The reason for the departure from linearity before the adsorption of a complete layer of oxygen atoms is again due perhaps to the high activity of oxygen in alkaline solution.

Curves 1, 2 and 3 show the gradual development of stages c and b. The value of $\frac{b}{a}$ curve 3 is again too large to represent a capacity change alone. It is interesting to note that whereas in acid solution stages a and c of the anodic curve are separated by a capacity change section, in alkaline solution they tend to run together. In the case of the cathodic curves however, the oxygen removal and hydrogen deposition stages in alkaline solution are separated by a capacity change, while there is no such separation in acid solution.

It is now necessary to examine why it is that only monatomic layers of hydrogen and oxygen are involved in the anodic and cathodic processes. The electrode remains at about the reversible electrode potential after a cathodic polarisation, thus it must be in equilibrium with the gaseous hydrogen present in the solution. At the reversible hydrogen electrode we have the following equilibrium:-



between the hydrogenions in solution, the hydrogen atoms adsorbed on the electrode surface and gaseous hydrogen. On making the electrode anodic, we see that the potential can be maintained provided that the molecular hydrogen can be adsorbed rapidly enough to replace those adsorbed atoms which have been desorbed as ions. If this process takes place rapidly, then more than an atomic layer of hydrogen atoms would have to be removed from the electrode surface before the potential was forced towards that at which the deposition of oxygen takes place.

The equilibrium conditions of the reversible hydrogen electrode have been studied by Butler⁽¹⁴⁾. If x , is the fraction of adsorption positions at the electrode surface occupied by hydrogen, then $k x^2$ represents the rate of desorption, while the rate of adsorption (which is proportional to the probability of finding two adjacent adsorption places vacant) is

$k_1'(1-x)_{\text{pH}_2}^2$. Hence at equilibrium we have

$$k_1 x^2 = k_1'(1-x)_{\text{pH}_2}^2$$

When hydrogen is being liberated at the electrode the equilibrium is disturbed and we have

$$i = k_1 x^2 - k_1'(1-x)_{\text{pH}_2}^2 \quad \text{-----(2)}$$

where i , is the rate of formation of hydrogen. If k_1 is larger compared with i the displacement of the adsorption equilibrium is small. Also the rate of formation of hydrogen cannot exceed k_1 .

Considering the equilibrium between the adsorbed hydrogen and the ions in solution, let k_0 be the rate of transfer of protons at the equilibrium potential V_0 to a completely unoccupied surface ($x = 0$). Let k_0' be the rate of transfer of hydrogen atoms to the solution as ions from a completely occupied surface ($x = 1$). The equilibrium condition is $k_0(1-x) = k_0'x$, at potential V_0 . When the potential is displaced by an amount ΔV from V_0 , these rates become $k_0(1-x)e^{-\varepsilon\Delta V/\gamma kT}$ and $k_0'xe^{\varepsilon\Delta V/\gamma kT}$, and the current is:-

$$i = k_0(1-x)e^{-\varepsilon\Delta V/\gamma kT} - k_0'xe^{\varepsilon\Delta V/\gamma kT}$$

where x is determined by (2)

From the above the following conclusions can be drawn.

(1) When i is small compared with k_1 , the adsorption equilibrium is not appreciably disturbed by the current and $-\Delta V$ varies linearly with the current.

(2) As i approaches k_1 , $(1 - x)$ approaches zero and therefore $-\Delta V$ will increase more rapidly than in case (1).

(3) When $i > k_1$, this mechanism is no longer capable of accounting for the whole of the current and the potential of the electrode must rise until some other process becomes possible, e.g. Gurney's mechanism.

Suppose we have an electrode, whose surface is free from adsorbed hydrogen immersed in a solution of sulphuric acid, also free from hydrogen. On making such an electrode cathodic with a large current the transference of hydrogen ions to adsorption positions takes place, in the course of which neutralisation occurs. This process can occur at any rate since the activation energy of the process is determined to some extent by the electrode potential, the more negative the potential the smaller the activation energy. The electrode potential is determined by the current density, thus k_0 is a function of the current density. The value of k_1 which determines the rate of desorption of adsorbed hydrogen atoms as hydrogen molecules is a fixed quantity and is relatively small. With large cathodic currents therefore, all the adsorption positions are occupied before an appreciable amount of hydrogen can be liberated by the above mechanism. As the adsorption positions are filled up the electrode becomes more negative until finally a point is reached at which some other process becomes possible, e.g. the discharge of hydrogen ions by Gurney's mechanism

We can also see why it is that on making the electrode anodic with a large current, after an initial cathodic, that the amount of hydrogen removed only corresponds to one atomic layer. Even although the electrode may have gaseous hydrogen on its surface, the rate of adsorption to give atomic hydrogen is limited by k_1 . As this constant is very much smaller than the current no appreciable adsorption takes place.

An examination of the curves shows that a linear relationship exists between the potential of a platinum electrode and the amount of hydrogen (or oxygen) adsorbed on it. The explanation may be that the heat of adsorption decreases according to a linear law as the surface is filled up. Becker⁽²⁵⁾ has shown that the rate of evaporation of oxygen atoms from a tungsten filament increases very rapidly with the amount of surface covered. This shows that the heat of adsorption must decrease as the surface concentration increases. A similar state of affairs may, therefore, hold for hydrogen and oxygen atoms on platinum. If this were so, then the observed relationship between the potential and the amount adsorbed would be accounted for, if the heat of adsorption decreased linearly with the amount adsorbed.

An alternative explanation may be that the adsorbed atoms behave as dipoles, there would then be a potential

difference proportional to the number of adsorbed atoms superimposed on the normal potential difference between the electrode and the ionic layer in the solution.

SUMMARY.

A study has been made of the anodic and cathodic polarisation of platinum electrodes in nitrogen saturated sulphuric acid and sodium hydroxide solutions at current densities between 200×10^{-3} and $4,000 \times 10^{-3}$ amps.

In sulphuric acid solution the anodic process has been shown to consist of the removal of a layer of atomic hydrogen followed by a capacity change and finally the deposition of a layer of atomic oxygen. The cathodic process is believed to be the reverse of the above, except that there is no capacity change effect between the removal of the adsorbed oxygen and the deposition of the layer of hydrogen.

A similar mechanism has been found to hold for the behaviour of platinum in sodium hydroxide solution. The cathodic curve taken after an initial polarisation with a small current shows the existence of a capacity change between the oxygen removal and hydrogen deposition processes.

The results of the experiments prove that the adsorption of a layer of atomic hydrogen precedes the establishment of the hydrogen overvoltage. It is suggested that the mechanism whereby the adsorption takes place is similar to that put forward by Butler. The continuous discharge of hydrogen once the overvoltage has been established is assumed to take place by a mechanism similar to that put forward by Gurney.



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PART II

THE ANODIC PASSIVATION OF GOLD

IN

HYDROCHLORIC ACID SOLUTION.

INTRODUCTION.

A metal is described as passive, when it ceases to dissolve or dissolves very slowly while acting as the anode in an electric circuit or when treated with chemical reagents. Conversely it is described as active if under the same conditions it is vigorously attacked.

The phenomena was first discovered by Keir in 1790.⁽¹⁾ Keir observed that iron after treatment with concentrated nitric acid, lost the power of precipitating silver and copper from solutions of their salts, also that it was no longer attacked by dilute nitric acid. The active condition was restored by scratching, contact with ordinary iron, or by a light blow. This phenomena was rediscovered by Wetzlar in 1827.

The next important contribution to this subject was made by Schonbein⁽²⁾ who incidentally introduced the terms "activity" and "passivity". Schonbein

showed that iron could be made passive by making it the anode of a cell in which oxygen acids were used as electrolytes - so called "anodic polarisation".

Faraday's name is also associated with the early development of the subject. He put forward the view that the phenomena was due to the formation of a film of oxide on the electrode surface.⁽³⁾ Faraday's theory held its own until Hittorf⁽⁴⁾ showed by his work on chromium that it had to face considerable difficulties, and that the properties of an oxide responsible for passivity would need to be different from those of any known oxides of the metal.

Since the beginning of the present century many investigations and extended researches have been carried out, the results of these may be summarised as follows:-

(1). Though the passive state is best known in connection with iron, cobalt, nickel and chromium, most other metals can be made to show this state.

(2). That passivity is induced by various oxidising agents i.e. HNO_3 , H_2CrO_4 , and HClO_3 ; by alkali hydroxides, and by anodic polarisation in a variety of electrolytes.

(3). That the passivated metal returns to the active state sooner or later, when the force inducing passivity is removed.

(4). That rubbing or scratching destroys passivity. Treatment with acids, particularly the halogen acids,

cathodic polarisation, and heating favour the active state.

(5). On anodic polarisation the metal becomes much more positive and either dissolves relatively slowly, or in a different ionic state, or not at all, when the equilibrium potential is reached. When the metal itself does not dissolve, the anion or oxygen is discharged instead.

(6). The nature of the anion has a considerable specific influence on passivation.

As to the explanation of the above facts considerable difference of opinion exists, and a number of theories have been put forward with a greater or less degree of recognition. The oxide theory of Faraday is believed by most authorities to be the most feasible. The alteration in the chemical properties of iron and other metals, when they become passive has also been attributed to a change in the electronic structure of the metal, thus iron which in the normal state has a 2,8,14,2, configuration, is supposed to change to 2,8,8,8, on passivation, giving a rare gas structure.

According to yet another theory, the passive state is supposed to be the normal state, but the metal is rendered active by the presence of a catalyst, which must therefore be removed before the metal becomes passive.

Many have hesitated to accept the oxide theory

because (1), in many cases no oxide film is visible when the metal is passive, and (2), because iron which is covered by a visible oxide film as a result of heating, is often not passive. On general grounds however, it seems at least possible that the production of passivity of iron by immersion in a solution of oxidising agents or by anodic treatment may be due to a film too thin to be visible^{or} to give rise to interference colours. Indeed it is clear that the greater the specific protective character of the material composing the film the less likely it is to reach a thickness which would make it visible, since the film will hinder its own growth, by excluding the oxidising material from the metal below. It is only when the protective character of the material is imperfect is a visible film to be expected. Thus it can be concluded that an efficient protective film will always remain invisible as long as it is in optical contact with the highly reflecting metal beneath. U.R.Evans,⁽⁵⁾ has succeeded in isolating the oxide film responsible for the passivity of an iron anode in a solution of dilute sulphuric acid. Evans was however unable to obtain a film from iron which had been passified by nitric acid. Hedges⁽⁶⁾ has however, made a comprehensive study of the passivation of iron by nitric acid, and this classical case has been brought into line with the oxide theory.

The anodic passivation of iron has been studied in detail by W.J.Müller^(?) in a quantitative manner. An essential feature of the experimental conditions is the elimination of disturbances at the anode due to convection currents. By the use of a horizontally disposed electrode, or shielded electrode, in place of the usual vertical electrodes, the products remain where they are formed.

Müller's experimental method is to observe the change of current density with time. One of the first results of this method was the demonstration that passivation is a time phenomena, and that the larger the current density the shorter the time required for passivation. In the case of iron in sulphuric acid solution the view is developed that FeSO_4 , a product of the reaction at the anode, accumulates at the anode surface until the solution in the immediate vicinity of the electrode becomes supersaturated. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is then deposited on the electrode surface. This deposit covers a large area of the electrode, and causes a large increase of the current density at the exposed portions, with a consequent rise in the anode potential there. The film of sulphate is not identified with that causing passivity, but by screening off a large part of the anode surface, it may give rise to conditions which cause true passivity. Müller

calls the first stage "Bedeckungs passivität" and the second "Chemisch passivität". This increase in the current density causes the anode potential to rise to a value at which reactions characteristic of the passive state can take place, namely some change in the electronic structure of the metal, so that it goes into solution as Fe^{+++} . The product is easily hydrolysed and forms a protective film of ferric oxide on the anode. This film gives rise to true passivity.

Müller further deduced theoretically a relation between the growth of the deposit and the fall of current, which is found to agree with the experimental results. Assuming that the film grows sideways only and the thickness remains constant, the change of the current i with time t , is given by:-

$$t = C + A \left(\frac{1}{i_0 - i} + \frac{2.3}{i} \log \frac{i_0 - i}{i - i_r} \right)$$

where i is the initial current, i_r the residual current, C and A are constants whose values can be calculated

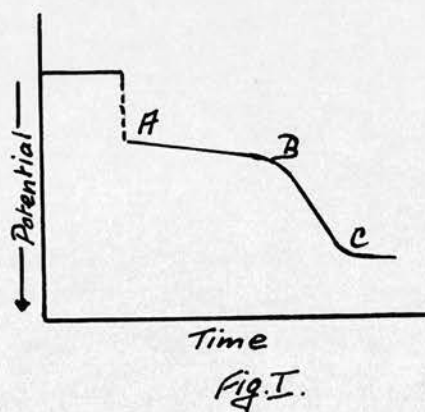
This sideways growth relation holds for iron in sulphuric acid in the early stages. In the later stages of the anodic polarisation, the film grows in thickness without sideways extension. Then the currents i_1 and i_2 passing at times t_1 and t_2 are in accordance with the formula:-

$$t_2 - t_1 = B \left(\frac{1}{i_1^2} - \frac{1}{i_2^2} \right)$$

where B is a constant depending on the area uncovered.

Like previous investigators who have discussed the problem qualitatively only, Muller regards the passivating film as being of a porous nature. He has shown quantitatively how the potential assumed by the metal is related to the number and size of these pores. The activating influence of chlorides is traced to the ease with which such small ions can travel through the pores of the film, while the larger anions such as SO_4^{--} and PO_4 can penetrate them only with difficulty.

Experiments on the anodic passivation of gold in hydrochloric acid solution have been carried out by Shutt and Walton⁽⁸⁾ under vastly different conditions from those prevailing in Muller's experiments. In these experiments the formation of a solid precipitate at the electrode was rendered impossible by vigorous stirring. Instead of observing the change of current with time, these authors applied a constant current to the electrode and observed the change of electrode potential with time. A typical curve of anode potential against time is shown in fig.I



A represents the potential attained immediately the current is switched on. This is followed by a steady fall of potential to the point B. Beyond this point the potential falls rapidly to C at which potential the full chlorine overvoltage is reached. The metal is now fully passive. Experiments of the above kind were carried out in various hydrochloric acid and mixed chloride solutions at current densities up to 2.5 amps/cm.² From these experiments the following points have been drawn.

(1), There is a limiting current density C_0 , below which no passivation occurs, and the gold is continually dissolved.

(2). The relationship between the passivation time, i.e. the time lapsing from the moment the current is switched on to that at which passivation is attained, and the current density takes the form

$$t = \frac{K}{C - C_0}$$

where t is the time of passivation, C_0 the limiting current density, C the actual current density. The value of C_0 was found to depend on the chlorine ion concentration, but not on the hydrogen ion concentration.

(3). The presence of oxidising ions does not facilitate the anodic passivation. This is surprising since it is to be expected that such ions would facilitate the formation of a protective oxide film.

Shutt and Walton conclude from their experiments that there are two distinct reactions taking place.

(1). Dissolution of the metal.

(2). The actual passivation reaction, with the evolution of chlorine.

According to the mechanism put forward by Shutt and Walton there is one stage in the passivation process which takes place slowly. This stage is assumed to be the adsorption of chloride ions on the metal surface. The velocity of adsorption on a fresh metal surface is proportional to the chlorine ion concentration, and this represents the maximum rate at which gold dissolution can take place. Thus C_0 is a measure of the maximum rate of chloride ion adsorption and consequently of gold dissolution. For current densities greater than C_0 , a second electrochemical process sets in. This is assumed to be the discharge of hydroxyl ions and the formation of an oxide film on the anode surface.

Butler and Armstrong⁽⁹⁾ take exception to the view that C_0 represents the maximum rate of adsorption of chloride ions on the electrode surface. It is pointed out that if Shutt and Walton's assumption is correct, K will represent the electrochemical equivalent of chloride ions adsorbed before passivation sets in, the actual value of K would represent the adsorption of many layers of chloride ions.

From their own results K is identified with the original amount of chloride ions near the electrode together with the amount which diffuses in before a constant diffusion layer is set up. The gold becomes passive when the chloride ion concentration near the electrode surface has been reduced to zero. A calculation of the thickness of the diffusion layer shows that it is of a value which is normally experienced in diffusion phenomena. The conclusion arrived at is that experiments on the passivation time throw no light on the actual passivation process .

It was, therefore, decided to extend the work of the above mentioned authors, and see if fresh data could be obtained which would enable one to decide between the opposing theories. Experiments on the time of passivation were, therefore, carried out with currents much larger than those used by Shutt and Walton. The passivation times were extremely small, in some cases less than $1/500$ th. of a second. It was thought that by reducing the passivation times to such a short interval the complicating diffusion effect would be eliminated or at least greatly reduced.

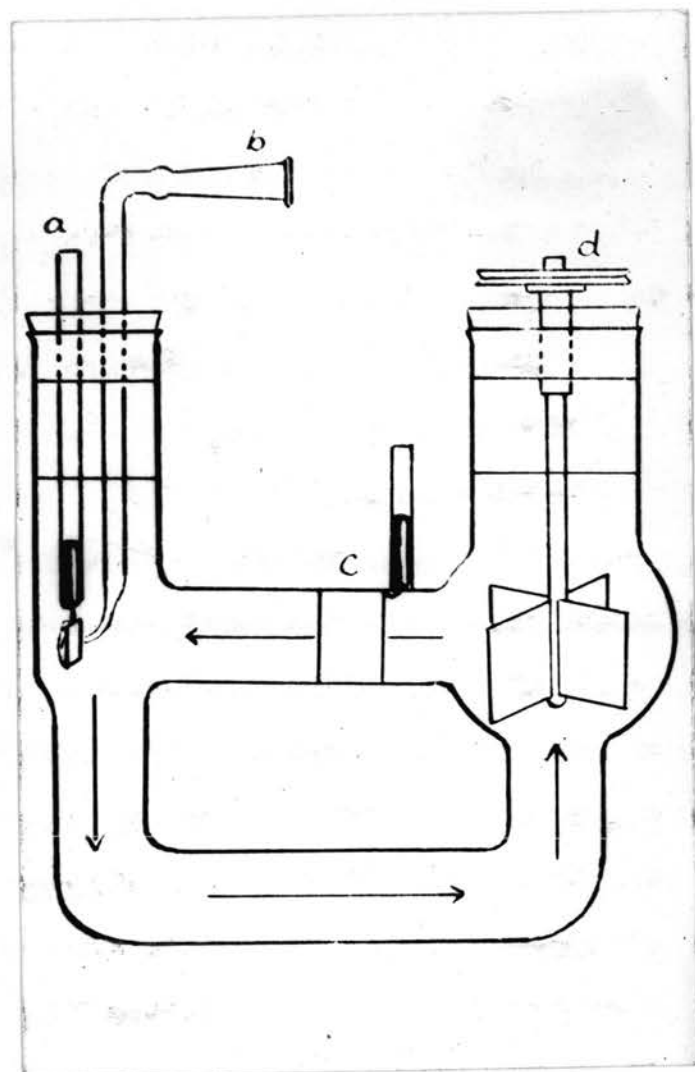


Fig II.

EXPERIMENTAL

The method used to record the rapid changes of electrode potential was similar to that previously described.

Electrolytic cell. Fig II shows the type of cell used. The test electrode a, had an exposed area of 0.5 sq.cm. (A few results were obtained with electrodes of 0.25 sq.cm., these have been corrected for the difference in area.) The electrodes were made by spot welding the gold foil to a gold wire sealed into the end of a piece of glass tubing. The back and sides of the electrode were covered with soft glass leaving one face exposed to the solution. Connection to the standard calomel electrode was made via the ground glass joint b. The auxiliary electrode c consisted of a cylinder of platinum foil. The solution could be stirred vigorously by the stirrer d, the solution impinging on the exposed face of the electrode. The tip of the standard calomel electrode was drawn out to a fine point so as to produce as little disturbance at the electrode as possible.

Preparation of the electrolytes. The various solutions were prepared from A.R. hydrochloric acid and water distilled in a pyrex apparatus.

Standard electrode. The electrode potentials were measured against a normal calomel electrode. The measured values of potential were reduced to the

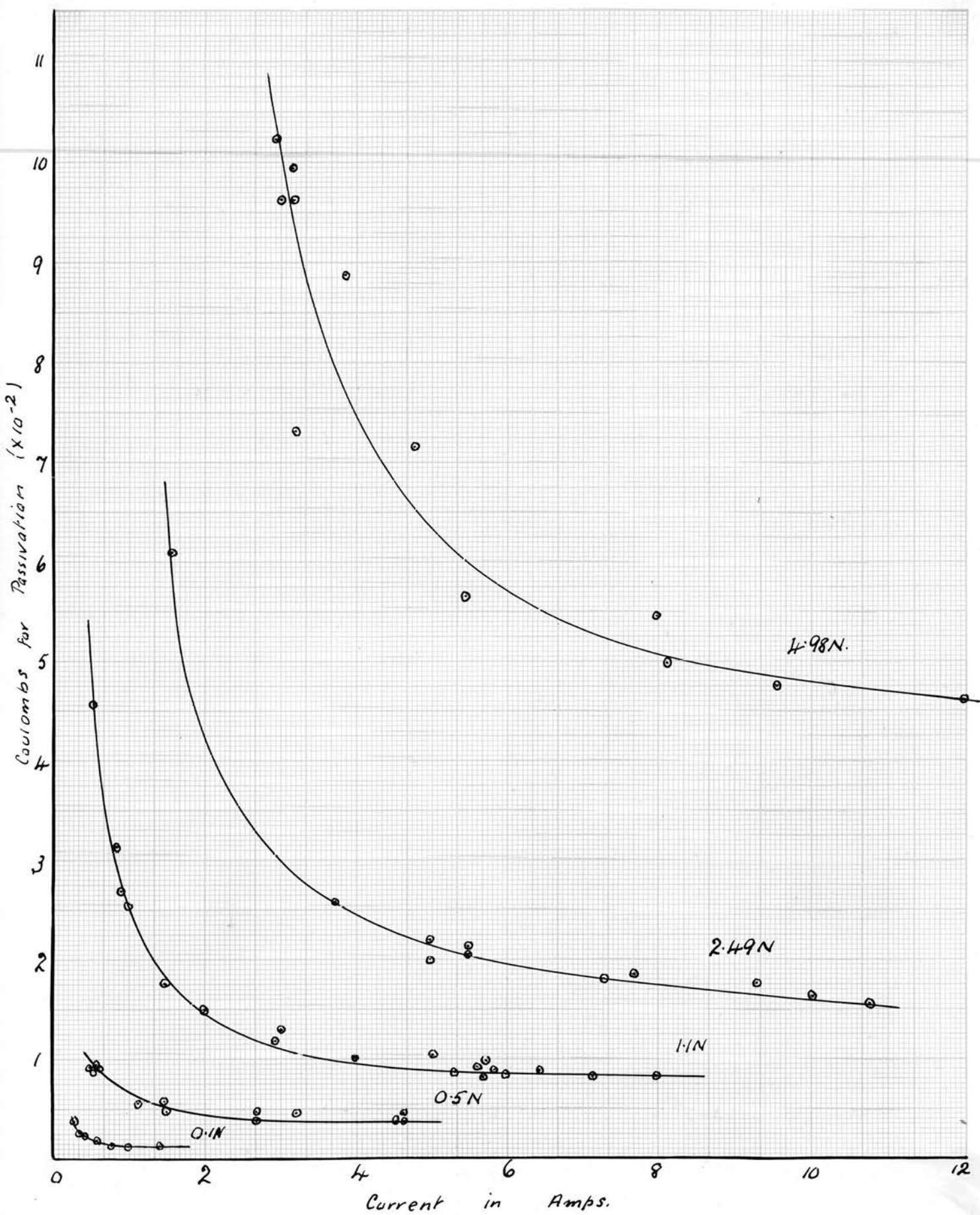


Fig. III.

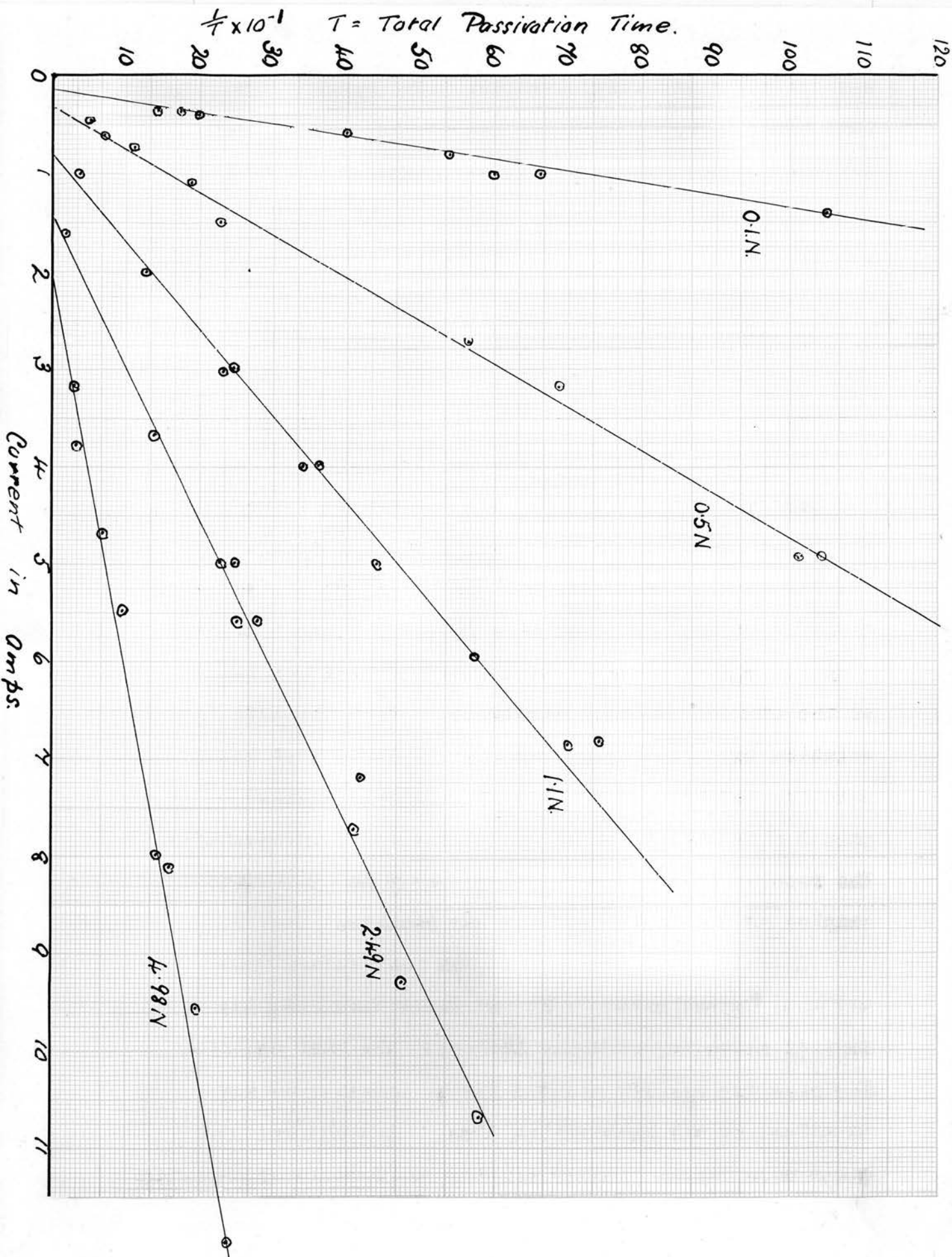


Fig. IV.

electrode was now fully passive. The passivation time T was measured from the instant the current was switched on to that at which the electrode became fully passive, i.e. to the point c . The passivation time was found to depend on the concentration of the hydrochloric acid solution and the current passed.

Measurements of the passivation time were made over a wide range of current densities in a series of hydrochloric acid solutions. These ranged from 0.1 N. to 4.98 N. In the case of individual solutions the current was pushed up to the maximum possible. The limiting factor in the case of the 0.1 N solution was its resistance. This not only limited the current which could be passed but also produced a large drop of potential between the test electrode and the tip of the standard calomel electrode. With the 4.98 N. solution the limiting factor was the heating of the solution and the electrode. The largest current passed with this solution was of the order of 24amps/cm.² The results obtained were reproducible and different samples of the metal gave similar results.

The effect of stirring on the passivation time was also investigated. It was found that with the smaller currents, stirring increased the time required for passivation, but with the larger currents it had no effect on the passivation time. All the results given were obtained under conditions of vigorous stirring.

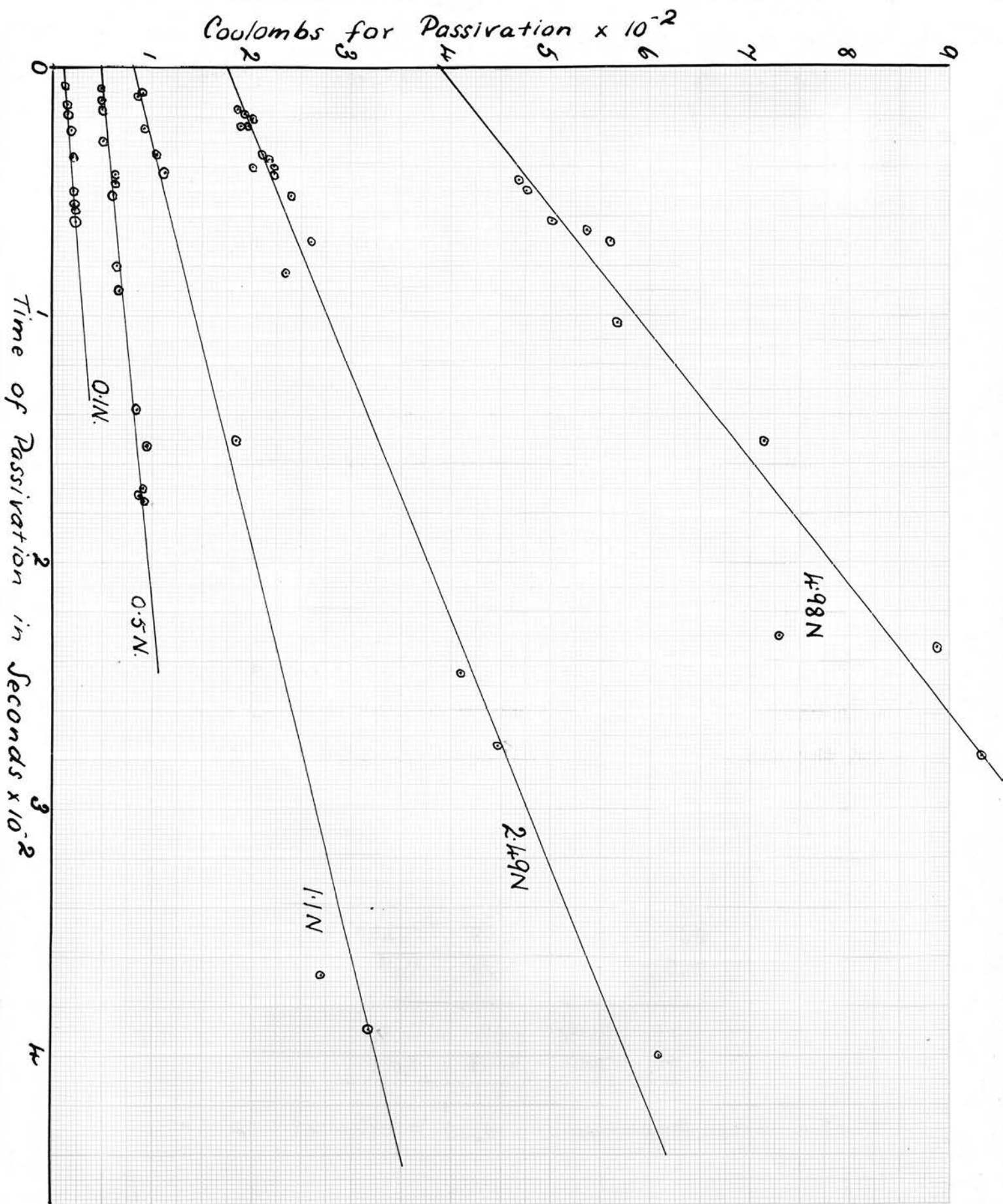


Fig. V.

Fig.III shows the relationship between the quantity of current required for passivation iT and the current i passed. The figures are for electrodes of 0.5 sq.cm. From fig.IV we see that the current i is proportional to $1/T$, and that this holds at the highest currents. This verifies the equation given by Shutt and Walton namely that

$$(i - i_0) = K/T$$

where i_0 is the limiting current density, i.e. the least current required to produce passivation, and K is a constant.

From fig.IV the values of i_0 for the various solutions were obtained. These are tabulated in table I. The slopes on the curves give the values of K for the different solutions, these are tabulated in table II. As a check, a plot was made of iT against T , fig. V, and the values of K and i_0 obtained are given in the respective tables.

Table I

N	i_0^* amps	i_0^+ amps	i_0 (mean) amps
0.1	0.15	0.18	0.165
0.5	0.30	0.24	0.27
1.1	0.80	0.62	0.71
2.49	1.40	1.00	1.20
4.98	2.10	1.98	2.05

i_0^* obtained from fig.IV. i_0^+ obtained from fig.V.

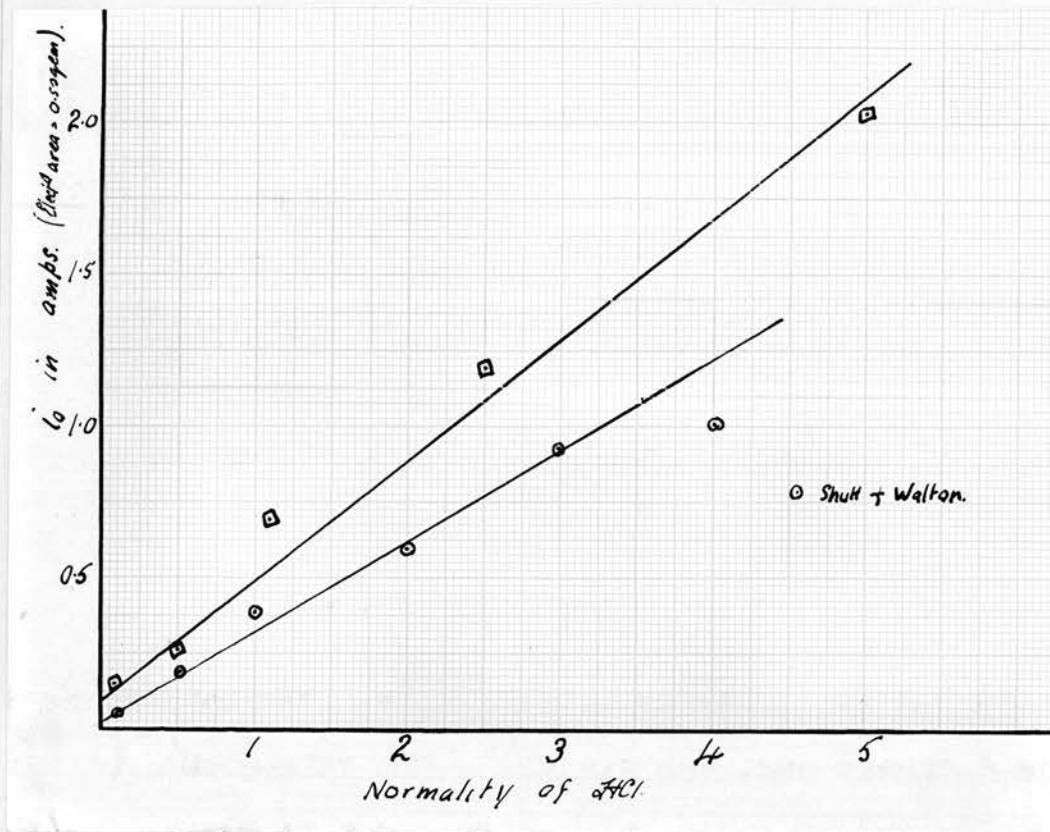


Fig. VI.

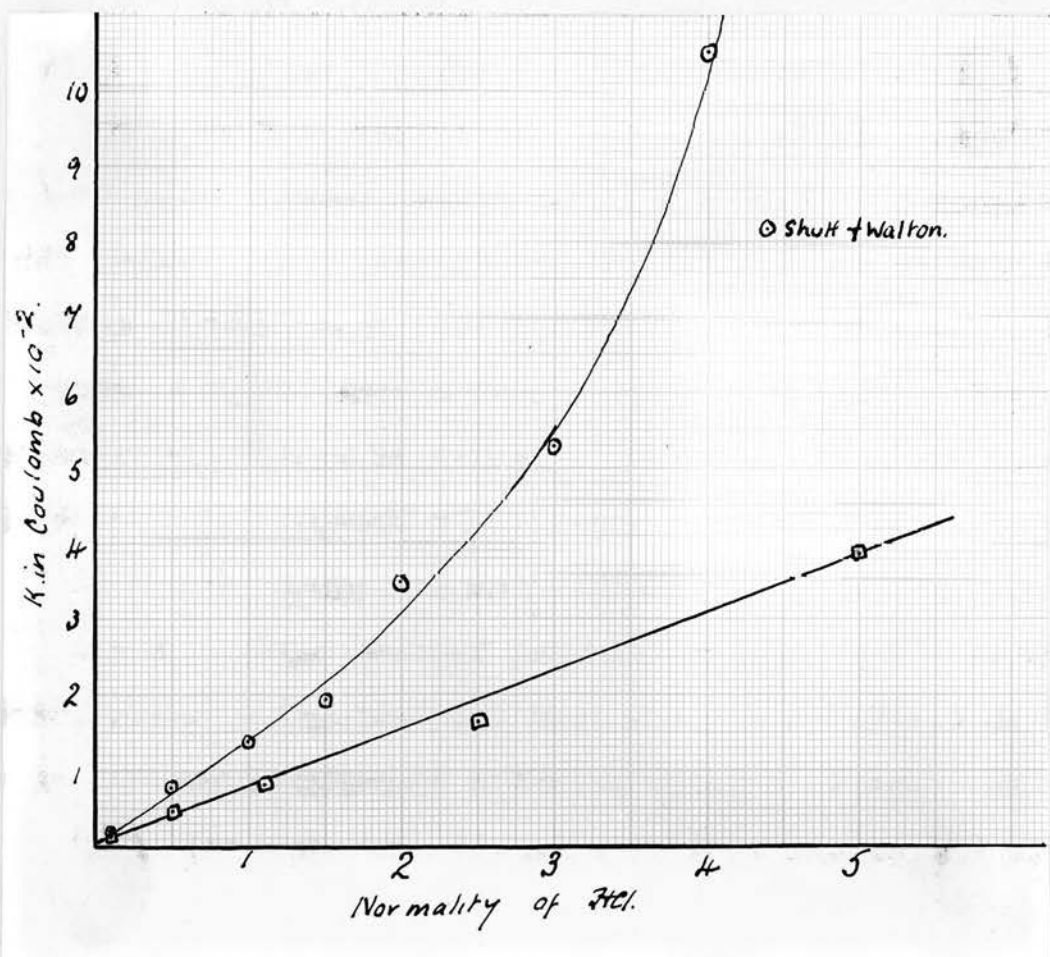


Fig. VII.

Table II

N	K^+_{Coults}	K^+_{Coults}	$K(\text{mean})_{\text{Coults}}$
0.1	1.25×10^3	1.20×10^3	1.20×10^3
0.5	4.75 --	4.60 --	4.67 --
1.1	8.00 --	9.20 --	8.60 --
2.49	1.75×10^2	1.60×10^2	1.67×10^2
4.98	3.85 --	4.00 --	3.92 --

 K^+ from fig.V. K^+ from fig.IV.

The relationship between i_0 and the acid concentration is a linear one, see fig VI. The values of i_0 determined by Shutt and Walton are also shown. Fig.VII shows that there is also a linear relation between K and the hydrochloric acid concentration. The values of K determined by Shutt and Walton are also given. It is seen that the values of K at the higher acid concentrations differ considerably from those obtained by Shutt and Walton. The reason for this may be due to the different experimental method used. Shutt and Walton used a commutator to make and break the current, a series of oscillograms being taken one after the other. In the present series of experiments however, only one oscillogram was taken at a time with a five minute interval between each. Shutt and Walton have shown that increasing the temperature increases K . It is possible therefore that the discrepancy in the values of K at high acid concentrations is

due to a heating of the solution or the electrode
by taking a series of oscillograms in rapid succession.

DISCUSSION.

The results obtained from the experiments just described show that the equation $(i - i_0)T = K$ holds up to the highest current densities it was possible to employ. Cutting down the passivation time has, therefore, resulted in no modification of the anodic process. If the actual passivation process with the smaller currents is obscured by a diffusion phenomena, increasing the current density to the maximum practical value, still leaves the process obscured. From this it appears that an essential feature of the passivation process is the reduction of the chloride ion concentration at the electrode surface to zero or nearly so, before passivation takes place. This reduction may take place as a result of gold dissolution, probably as AuCl_4^- . When the chloride ion concentration has been sufficiently reduced the passivation process then commences.

Experiments on the anodic oxidation of gold in sulphuric acid solution by Armstrong and Butler⁽¹⁰⁾ have shown that oxygen is first deposited on the electrode in an adsorbed condition and a definite oxide is formed by the rearrangement of the (AuO_x) surface layer. It is reasonable to suppose that some such process is responsible for passivation in chloride solution. The discharge of chloride ions which have diffused through the diffusion layer will, however,

occur concurrently with the passivation process.

It is now necessary to see if the quantity of current passed before passivation sets in is of the order required to set up a diffusion layer at the electrode surface. The value of K may be taken to represent the quantity of current required to set up a diffusion layer, this value will include the amount of current required to discharge those chloride ions which diffuse in while the layer is being set up. The thickness of the layer may be obtained from the expression,

$$K = \frac{c\delta F}{2 \times 1000}$$

where c is the concentration of hydrochloric acid, δ (in cm.) the thickness of the diffusion layer and F the electrochemical equivalent.

From table III we see that the thickness of the diffusion layer remains practically the same for all concentrations of hydrochloric acid. The values of δ are also of a magnitude normally found in diffusion phenomena associated with the dissolution of solids under conditions of vigorous stirring.

The removal of chloride ions at the electrode has been assumed to be by the dissolution of gold and the formation of AuCl_4^- ions. The reaction at the electrode is,



Table III

N	2K coul.	δ in cm.	2i amp.	δ in cm.
0.1	2.4×10^{-3}	4.8×10^{-4}	0.37	6×10^{-4}
0.5	9.3 --	3.7 --	0.54	1.8×10^{-3}
1.1	1.72×10^{-2}	3.2 --	1.42	1.5 --
2.49	3.3 --	3.6 --	2.40	2.0 --
4.98	7.8 --	3.2 --	4.10	2.4 --

From this equation the thickness of the diffusion layer may also be calculated. During the passage of 3 faradays 4 equivalents of chloride ion react with the gold. The rate of removal of the chloride ion at the surface in this reaction is $4i/3F$ equivs. per sec. If N_a is the transport number of Cl^- then the rate at which chloride ions are carried up to the surface is iN_a/F . Hence $i(4/3 - N_a)/F$ is the net rate of depletion. The limiting current i_0 which corresponds to the rate of diffusion to the electrode in the steady state is thus equivalent to a rate of diffusion of $i_0(4/3 - N_a)/F$. Let δ be the thickness of the diffusion layer and assume a constant diffusion gradient. Let c be the concentration of chloride ion in the bulk of the solution and assume the concentration of chloride at the electrode to be zero. The diffusion gradient is therefore, c/δ , and the diffusion rate Dc/δ , where D is the diffusion coefficient. Thus:-

$$Dc/\delta = i_0(4/3 - N_a)/F$$

D is taken as $2 \times 10^{-5} \text{ cm}^2/\text{sec.}$, F is 5×10^5 coulombs. $(4/3 - Na)$ may be taken as unity. The values of α obtained from this equation are also given in table III, and are in reasonably good agreement with those obtained by the first method. It may be mentioned here, that the temperature coefficient observed by Shutt and Walton is of the order of 0.03, which is of the magnitude of those commonly met with in diffusion phenomena.

The problem of the setting up of a diffusion layer at the surface of an electrode has been studied by Sand⁽¹¹⁾. He has determined how the concentration of depolariser at the electrode surface varies with time and the current density, from that in the bulk of the solution.

The electrode is supposed to be placed to be in a stationary solution of a depolariser which extends infinitely in a direction normal to its surface. If a constant current is passed, then the problem may be treated by a modification of Ficks Law. If c be the concentration of the reactant at a distance x from the electrode, then the variation of c with the time t is,

$$dc/dt = K d^2c/dx^2 \text{ -----(1)}$$

where K is the diffusion coefficient of the reacting substance. Sand now makes the assumption that the rate of diffusion per unit area, $K(dc/dx)$, immediately

at the electrode surface, where $x = 0$, is equal to the rate at which the depolariser is being used up and so is proportional to the current density i . The differential equation can now be solved for $x = 0$, so as to give the variation of the concentration of the depolariser at the electrode surface with the time. The solution to this equation obtained by Sand is:-

$$c = c_0 - 1.13/96500 (1 - N_a)i\sqrt{t}/K \quad \text{---(2)}$$

where c_0 is the concentration of the reactant in the bulk of the solution and N_a the transport number of the anion.

This equation simplifies to,

$$c = c_0 - k i \sqrt{t}/K \quad \text{---- (3).}^*$$

If we put $c = 0$, then the time taken for the concentration of the reactant at the electrode surface to fall to zero can be obtained

$$\begin{aligned} c_0 &= k \sqrt{t}/K \\ \text{or } t &= k' (c_0/i)^2 \end{aligned}$$

where $k' = (k/K)$.

Thus if we carry out a series of determinations of t at different current densities in the same solution, i.e. for $c_0 = \text{const.}$, then,

$$1/t \propto i^2$$

The experimental result which we have obtained is,

$$1/t \propto i.$$

Sand has however made the assumption that $i = Kdc/dx$

* Assuming that no depolariser is brought up to or removed from the electrode by ionic transport.

at the electrode. This assumes that dc/dt at the electrode is relatively small. It is doubtful if this is fulfilled in these experiments. If the necessary correction is made to the differential equation (1) its solution becomes extremely difficult. But at least it can be concluded that the Sand result is not necessarily fatal to the attribution of the observed effects to a diffusion phenomena.

Summary.

A study of the time of passivation of gold has been made in a series of hydrochloric acid solutions. For a given concentration of hydrochloric acid the equation $(i - i_0)T = K$ holds for all current densities provided the solution is vigorously stirred. This equation is similar to that obtained by Shutt and Walton working at lower current densities.

A linear relation has been found to exist between i_0 , the limiting current density and the acid concentration. A similar relation also holds between the constant K and the hydrochloric acid concentration.

The results obtained have been interpreted on the basis of a diffusion theory. The time of passivation is taken to be the time required to set up a diffusion layer at the electrode surface. The reduction of the chloride concentration at the electrode surface to nearly zero is assumed to be necessary before the passivation of the electrode can take place.

Two methods have been given whereby the thickness of the diffusion layer at the electrode can be determined. The results are in reasonable agreement with each other and are of the order normally encountered in diffusion phenomena.

A reason for the non-application of Sand's equation has been suggested.

In conclusion, I would like to express my thanks to Dr.J.A.V.Butler for his continued interest in the work and helpful criticism during the course of the research.

I have also to thank the Royal Society for a grant towards the purchase of apparatus.

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